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CHEMISTRY today

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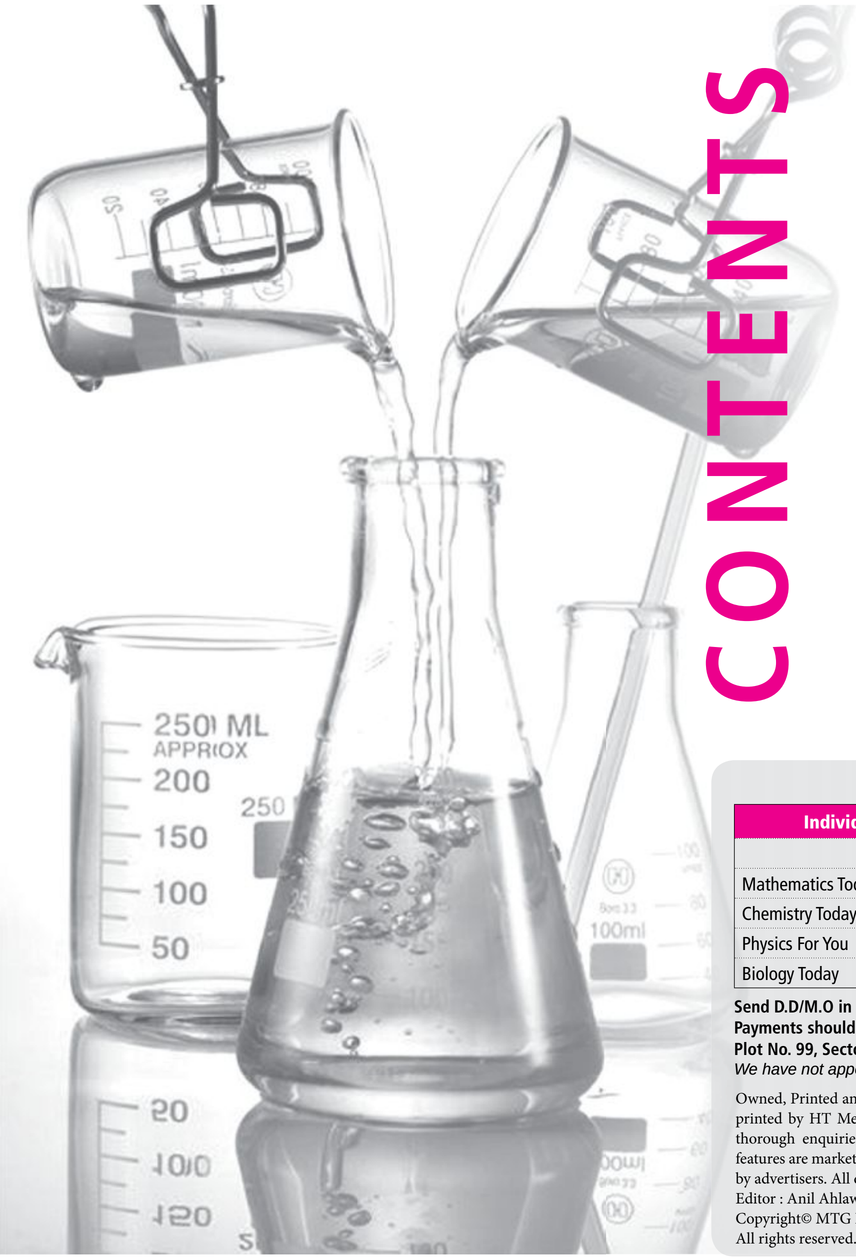

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NEET | JEE ESSENTIALS

Class XI

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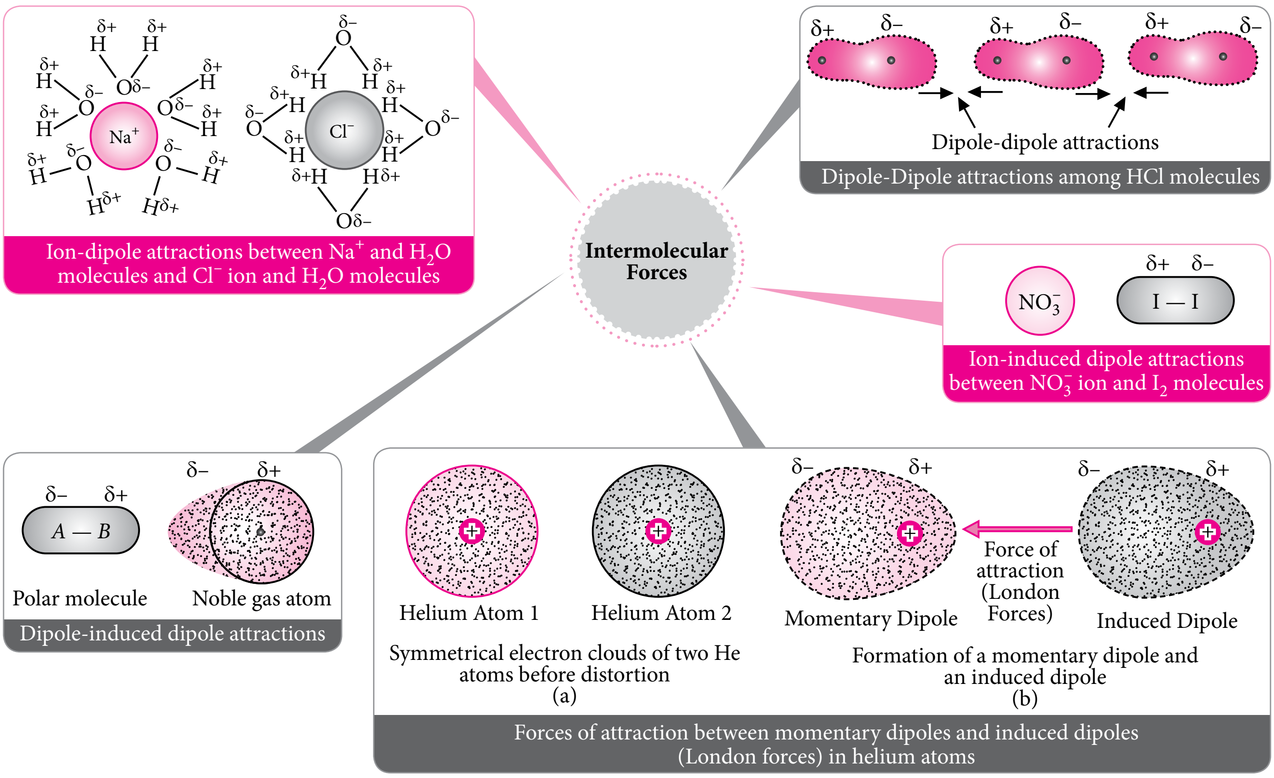
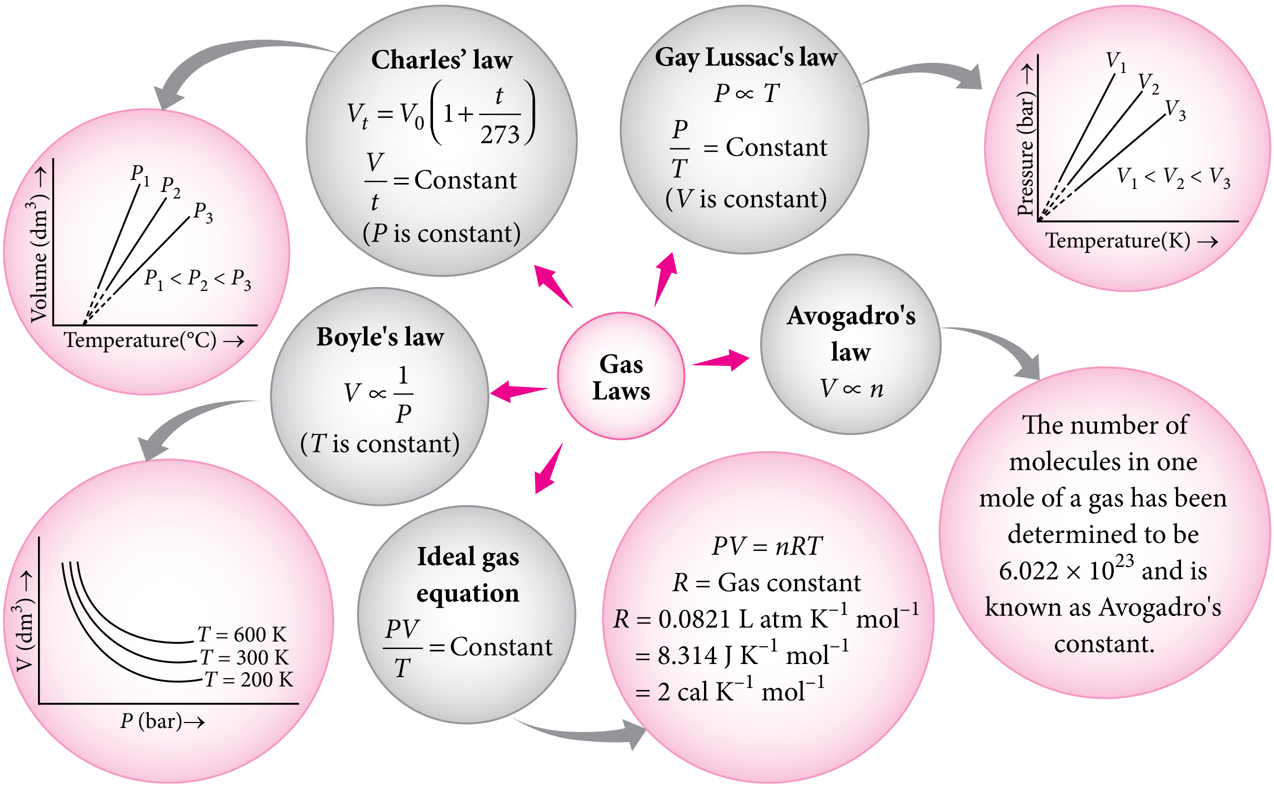
Unit 3 States of Matter : Gases & Liquids | Thermodynamics

STATES OF MATTER : GASES & LIQUIDS

Gaseous State of Matter





Dalton's Law of Partial Pressures

- The total pressure exerted by a mixture of two or more non-reacting gases enclosed in a vessel is equal to the sum of the individual partial pressures which each gas would exert when present alone in the same vessel at the same temperature.
  $P_{total} = p_1 + p_2 + p_3 + ... + p_n$
  $p_1 = x_1 P_{total}$
  x_1 = Mole fraction of the gas 1.

Graham's Law of Diffusion / Effusion

- Under similar conditions of temperature and pressure, the rates of diffusion/effusion of different gases are inversely proportional to the square root of their densities.
  $$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$
  where d_1, d_2 are densities of two gases.
  $$\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{d_2}{d_1}} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$
  $$\frac{r_1}{r_2} = \sqrt{\frac{T_1\, d_2}{T_2\, d_1}} = \sqrt{\frac{T_1\, M_2}{T_2\, M_1}}$$

Kinetic Molecular Theory of Gases

- The molecules are separated from one another by large distances.
- Molecular collisions are perfectly elastic.
- There are no forces of interactions between the molecules.
- Kinetic gas equation, $PV = \frac{1}{3}mn\bar{u}^2$

  where, P = Pressure exerted by the gas,
  m = Mass of each molecule of gas,
  n = Total number of molecules of the gas present in volume V,
  $\bar{u}$ = Root mean square speed of the gas

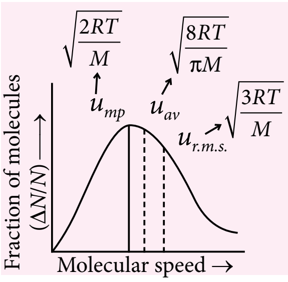
  K.E., $E_k = \frac{3}{2}nRT$

  Average kinetic energy, $\bar{E}_k = \frac{1}{2}m\bar{u}^2 = \frac{3}{2}\frac{RT}{N_A}$

  where, N_A = Avogadro's constant
- The average kinetic energy of gas molecules is directly proportional to the absolute temperature of the gas.
- All gases are made up of a very large number of molecules.

Maxwell-Boltzmann Distribution of Molecular Speeds

- The plot between the fraction of molecules ($\Delta N/N$) possessing particular speeds against their corresponding speeds at a particular temperature is known as Maxwell's distribution curve.



$u_{mp} : u_{av} : u_{rms} = 1 : 1.128 : 1.224$

Deviation from Ideal Gas Behaviour

- Real gases do not follow ideal gas equation perfectly at all conditions of temperatures and pressures.
- $\frac{PV}{nRT} = Z =$ Compressibility factor
  - For an ideal gas, $Z = 1$
  - For a real gas :
    $Z > 1$ (Positive deviation)
    $Z < 1$ (Negative deviation)
- **Equation of state for real gases (van der Waals' equation) :**

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where, a and b are van der Waals' constants.

Liquefaction of Gases

- Gases can be liquefied by decreasing temperature or increasing pressure.
- **Critical pressure :** The minimum pressure required to liquefy a gas at its critical temperature.

$$P_c = \frac{a}{27b^2}$$

- **Critical volume :** Volume occupied by one mole of a gas at its critical temperature and pressure.

$$V_c = 3b$$

- **Critical temperature :** A temperature above which a gas cannot be liquefied however high pressure may be applied on the gas.

$$T_c = \frac{8a}{27Rb}$$

Liquid State of Matter

- Liquids have definite volumes but not definite shapes.

Properties of Liquid State

- **Boiling point :** Temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure.
- **Surface tension :** Force per unit length acting perpendicular to the tangential line drawn at the surface of liquid is known as surface tension.

Surface Tension

- Surface tension causes
  - Rise of a liquid in a capillary tube.
  - Spherical shape of a drop
  - Liquid wet things.
- Unit : N m^{-1} or dyne cm^{-1}
- Surface tension decreases with increase in temperature.
- Greater the molecular forces, higher is the surface tension.

- **Viscosity :** Internal resistance to the flow in liquids.

$F = \eta A \frac{dv}{dx}$, where, A = Area,

$\frac{dv}{dx}$ = Velocity gradient,

η = Coefficient of viscosity,

INFO SHOTS

New state of matter !

A new form of matter, a supersolid, which combines the properties of solids with those of superfluids. By using lasers to manipulate a superfluid gas known as Bose-Einstein condensate was coaxed into a quantum phase of matter that has a rigid structure-like a solid and can flow without viscosity (like superfluids).

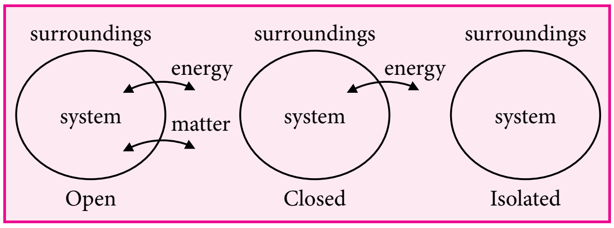
THERMODYNAMICS

- A specified part of the universe which is under thermodynamic consideration is called the system.

Thermodynamics Terms

- **Extensive properties :** Properties of the system whose value depends upon the amount or size of the substance present in the system *e.g.*, Gibbs free energy, enthalpy, entropy, internal energy, etc.
- **Intensive properties :** Properties of the system whose value is independent of the amount or size of the substance present in the system but depends only upon the nature of the substance *e.g.*, temperature, pressure, viscosity, etc.
- **State function :** A physical quantity is said to be a state function if its value depends only upon the state of the system and is independent of the path by which the state is reached *e.g.*, volume, temperature, internal energy, enthalpy.
- **Path function :** A physical quantity is a path function if it depends upon the path by which the change is brought about *e.g.*, work and heat.

Different Types of Systems



Types of Processes

- **Isothermal process**
  $\Delta T = 0$
  $q \neq 0$
- **Adiabatic process**
  $\Delta q = 0$
  No heat exchange
- **Cyclic process**
  A process in which the system undergoes series of changes and returns to its original state.
  ΔU or $\Delta H = 0$
- **Isobaric process**
  $\Delta P = 0$
- **Isochoric process**
  $\Delta V = 0$

First Law of Thermodynamics

Energy can neither be created nor destroyed, although it can be converted to one form to another form. The total energy of the universe remains constant.

$$\Delta U = q + w$$

where, ΔU = Change in internal energy;
q = heat change; w = work done

Sign Conventions

q = +ve (when heat is absorbed by the system)
q = –ve (heat is evolved by the system)
w = +ve (work is done on the system)
w = –ve (work is done by the system)

Work

- For isothermal reversible expansion,

$$q = -w = p_{ext}(V_f - V_i)$$
$$= nRT \ln \frac{V_f}{V_i}$$
$$= 2.303\ nRT \log \frac{V_f}{V_i}$$
$$= 2.303 nRT \log \frac{P_i}{P_f}$$

- For adiabatic reversible process, $q = 0$

$$\Delta U = w_{ad} = nC_v\Delta T = \frac{nR}{\gamma - 1}\Delta T$$

Enthalpy change (ΔH)
Heat absorbed or evolved (ΔH) during a reaction at constant pressure.

Internal energy change (ΔU)
The change in internal energy (ΔU) is the heat absorbed or evolved at constant volume.

$\Delta H = \Delta U + P\Delta V$
$\Delta H = \Delta U + \Delta n_g RT$
Δn_g = change in number of gaseous moles

Heat Capacity

It is the amount of heat required to raise the temperature of the system through 1°C
$C = q/\Delta T$

Heat capacity at constant volume (C_v)
$C_v = 3R/2$ (For monoatomic gas)
$C_v = 5R/2$ (For diatomic gas)

Heat capacity at constant pressure (C_p)
$C_p = 5R/2$ (For monoatomic gas)
$C_p = 7R/2$ (For diatomic gas)

$C_p/C_v = \gamma$

$C_p = C_v + nR$

Hess's Law

- The enthalpy change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.

$$AB_{(s)} \xrightarrow{\Delta_{sol}H^\circ} A^+_{(aq)} + B^-_{(aq)}$$

$$AB_{(s)} \xrightarrow{\Delta_{lattice}H^\circ} A^+_{(g)} + B^-_{(g)} \xrightarrow{\Delta_{hyd}H^\circ} A^+_{(aq)} + B^-_{(aq)}$$

$$\Delta_{sol}H^\circ = \Delta_{lattice}H^\circ + \Delta_{hyd}H^\circ$$

- Enthalpy of reaction = (Sum of bond enthalpies of reactants) – (Sum of bond enthalpies of products)
- Enthalpy of reaction = (Sum of enthalpies of products) – (Sum of enthalpies of reactants)

Entropy

- The property of a system which measures the degree of disorder or randomness in the system.

$$\Delta S = \frac{q_{rev}}{T}$$

$$\Delta S = nC_v \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} = nC_p \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

- For isothermal process, $\Delta S_t = nC_v \ln\frac{V_2}{V_1} = nC_p \ln\frac{P_1}{P_2}$
- For isochoric process, $\Delta S_v = nC_v \ln\frac{T_2}{T_1}$
- For isobaric process, $\Delta S_p = nC_p \ln\frac{T_2}{T_1}$
- $\Delta_{fusion}S^\circ = \frac{\Delta_{fusion}H^\circ}{T_f}$; $\Delta_{vap}S^\circ = \frac{\Delta_{vap}H^\circ}{T_b}$
- **Second law of thermodynamics :** The entropy of the universe is continuously increasing in the course of every spontaneous change.

Gibbs Free Energy

- $G = H - TS$, where, G = Gibbs free energy
- $\Delta G = \Delta H - T\Delta S$
- **Units :** kJ/mol, J/mol
- $\Delta G^\circ = \Sigma\Delta_f G^\circ_{(products)} - \Sigma\Delta_f G^\circ_{(reactants)}$
- $\Delta G^\circ = -2.303\ RT \log K_{eq}$
- $\Delta G = RT\ln\frac{V_1}{V_2} = RT\ln\frac{P_2}{P_1}$

Gibbs Free Energy

ΔG = –ve	ΔG = 0	ΔG = +ve
Spontaneous	At equilibrium	Non-spontaneous

- If ΔH = +ve; ΔS = +ve $\Rightarrow \Delta G$ = –ve if $T\Delta S > \Delta H$ (At high temperature)
- If ΔH = –ve, ΔS = +ve $\Rightarrow \Delta G$ = –ve (at all temperatures)
- If ΔH = –ve, ΔS = –ve $\Rightarrow \Delta G$ = –ve if $\Delta H > T\Delta S$ (at low temperature)

Third Law of Thermodynamics

- At absolute zero, the entropy of a perfectly crystalline substance is taken as zero. $S_0 = 0$
- The most important application of the third law of thermodynamics is that it helps in the calculation of the absolute entropies of the substances at room temperature (or at any temperature T). These determinations are based upon the heat capacity measurements.
- **Residual entropy :** The entropy possessed by a substance at absolute zero is called its residual entropy.

SPEED PRACTICE

1. The heat of combustion of benzene in a bomb calorimeter (*i.e.* at constant volume) was found to be 3263.9 kJ mol^{-1} at 25 °C. Calculate the heat of combustion of benzene (in kJ mol^{-1}) at constant pressure.
   (a) −3263.9 (b) −3267.6
   (c) −3260.2 (d) + 436.1

2. Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape?
   (a) 3/8 (b) 1/2
   (c) 1/8 (d) 1/4
   (NEET Phase-I 2016)

3. Calculate the heat required to raise the temperature of 60.0 g of aluminium from 35 to 55 °C. (Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.)
   (a) 1.07 kJ (b) 1.57 kJ
   (c) 1.07 J (d) 1.57 J

4. A gaseous mixture of 2 moles of *A*, 3 moles of *B*, 5 moles of *C* and 10 moles of *D* is contained in a vessel. Assuming that gases are ideal and the partial pressure of *C* is 1.5 atm, the total pressure is
   (a) 3 atm (b) 6 atm
   (c) 9 atm (d) 15 atm

5. The heat of reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$, at 27 °C was found to be −21.976 kcal. What will be the heat of the reaction at 50 °C? (The molar heat capacities at constant pressure for nitrogen, hydrogen and ammonia are 6.8, 6.77 and 8.86 cal mol^{-1} $degree^{-1}$ respectively.)
   (a) −22.192 kcal (b) −24.132 kcal
   (c) −21.760 kcal (d) −21.976 kcal

6. What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of oxygen at 0.7 bar are introduced in 1 L vessel at 27 °C?
   (a) 1.8 bar (b) 0.4 bar
   (c) 1.4 bar (d) 1.5 bar

7. Calculate Δ*H* at 85 °C for the reaction,
   $Fe_2O_{3(s)} + 3H_{2(g)} \longrightarrow 2Fe_{(s)} + 3H_2O_{(l)}$.
   Given : $\Delta H°_{(298\ K)} = -33.29$ kJ/mol and

Substance	$Fe_2O_{3(s)}$	$Fe_{(s)}$	$H_2O_{(l)}$	$H_{2(g)}$
C_p° (J/K-mol)	103.8	25.1	75.3	28.8

   (a) −28.14 kJ / mol (b) 35.9 kJ / mol
   (c) −303.29 kJ / mol (d) −25.1 kJ / mol

8. The average energy per molecule of a gas at a given temperature *T*, is given by
   (a) $\frac{3}{2}RT$ (b) $\sqrt{\frac{3RT}{M}}$
   (c) $\sqrt{\frac{8(R/N_A)T}{\pi M}}$ (d) $\frac{3}{2}\left(\frac{R}{N_A}\right)T$

9. What will be the entropy change for the reaction, $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ at 300 K? (Standard entropies of $H_{2(g)}$, $O_{2(g)}$ and $H_2O_{(l)}$ are 126.6, 201.20 and 68.0 J K^{-1} mol^{-1} respectively.)
   (a) −318.4 J K^{-1} mol^{-1} (b) 318.4 J K^{-1} mol^{-1}
   (c) 31.84 J K^{-1} mol^{-1} (d) None of these

10. For a given reaction, Δ*H* = 35.5 kJ mol^{-1} and Δ*S* = 83.6 J K^{-1} mol^{-1}. The reaction is spontaneous at (Assume that Δ*H* and Δ*S* do not vary with temperature.)
   (a) $T > 425$ K (b) all temperatures
   (c) $T > 298$ K (d) $T < 425$ K
   (NEET 2017)

11. Given : $C + 2S \longrightarrow CS_2$; Δ*H* = 117 kJ mol^{-1}
   $C + O_2 \longrightarrow CO_2$; Δ*H* = − 393 kJ mol^{-1}
   $S + O_2 \longrightarrow SO_2$ Δ*H* = −297 kJ mol^{-1}
   The heat of combustion of CS_2 to form CO_2 and SO_2 is
   (a) −1104 kJ mol^{-1} (b) 1104 kJ mol^{-1}
   (c) + 807 kJ mol^{-1} (d) −807 kJ mol^{-1}

12. Calculate the root mean square speeds of nitrogen at N.T.P.
   (a) 493×10^4 m/s (b) 493.13 m/s
   (c) 493×10^2 m/s (d) 493×10^3 m/s

13. An irreversible process taking place at constant P and T, in which only pressure-volume work is being done by the system, the change in Gibbs energy (dG) and change in entropy (dS), satisfy the criterion
(a) $(dS)_{V,U} = 0, (dG)_{T,P} = 0$
(b) $(dS)_{V,U} = 0, (dG)_{T,P} = +ve$
(c) $(dS)_{V,U} = -ve, (dG)_{T,P} = -ve$
(d) $(dS)_{V,U} = +ve, (dG)_{T,P} = -ve$

14. At 27 °C, 500 mL of helium diffuses in 30 minutes. What is the time (in hours) taken for 1000 mL of SO_2 to diffuse under the same experimental conditions?
(a) 240 (b) 3
(c) 2 (d) 4

15. 4 g of graphite is burnt in a bomb calorimeter of heat capacity of 30 kJ K^{-1} in excess of oxygen at 1 atmospheric pressure. The temperature rises from 300 K to 304 K. What is the enthalpy of combustion of graphite (in kJ mol^{-1})?
(a) 360 (b) 1440
(c) –360 (d) –1440

16. The r.m.s. velocity of hydrogen is $\sqrt{7}$ times the r.m.s. velocity of nitrogen. If T is temperature of the gas then
(a) $T_{(H_2)} = T_{(N_2)}$ (b) $T_{(H_2)} > T_{(N_2)}$
(c) $T_{(H_2)} < T_{(N_2)}$ (d) $T_{(H_2)} = \sqrt{7}\, T_{(N_2)}$

17. Among the following, the incorrect statement is
(a) at very large volume, real gases show ideal behaviour
(b) at very low temperature, real gases show ideal behaviour
(c) at Boyle's temperature, real gases show ideal behaviour
(d) at low pressure, real gases show ideal behaviour
(JEE Main Online 2017)

18. The volume of 0.0168 mol of O_2 obtained by decomposition of $KClO_3$ and collected by displacement of water is 428 mL at pressure 754 mmHg at 25 °C. The pressure of water vapour at 25 °C is
(a) 18.5 mm Hg (b) 20.6 mm Hg
(c) 22.3 mm Hg (d) 24.6 mm Hg

19. In which reaction, ΔS is positive?
(a) $H_2O_{(l)} \longrightarrow H_2O_{(s)}$
(b) $3O_{2(g)} \longrightarrow 2O_{3(g)}$
(c) $H_2O_{(l)} \longrightarrow H_2O_{(g)}$
(d) $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

20. The pressure of a fixed amount of an ideal gas is 0.75 N m^{-2}. What will be the pressure after the volume of the gas is tripled and the absolute temperature is doubled?
(a) 0.75 N m^{-2} (b) 0.25 N m^{-2}
(c) 0.50 N m^{-2} (d) 1.00 N m^{-2}

21. The following data are available for the melting of KCl : $\Delta H_{fus} = 7.25$ kJ mol^{-1} and $\Delta S_{fus} = 0.007$ kJ K^{-1} mol^{-1}. Calculate the melting point of KCl.
(a) 1035.7 K (b) 762.7 K
(c) 897.5 K (d) 1308.7 K

22. For gaseous state, if most probable speed is denoted by $\overset{*}{c}$, average speed by $\bar{c}$ and root mean square speed by c, then for a large number of molecules the ratio of these speeds are
(a) $\overset{*}{c} : \bar{c} : c = 1 : 1.128 : 1.224$
(b) $\overset{*}{c} : \bar{c} : c = 1 : 1.224 : 1.128$
(c) $\overset{*}{c} : \bar{c} : c = 1.224 : 1.228 : 1$
(d) $\overset{*}{c} : \bar{c} : c = 1.128 : 1.224 : 1$ **(JEE Main 2013)**

23. A reaction, $A + B \longrightarrow C + D + q$ is found to have a positive entropy change. The reaction will be
(a) possible at high temperature
(b) possible only at low temperature
(c) not possible at any temperature
(d) possible at any temperature.

24. Capillary action of the liquid can be explained on the basis of its
(a) resistance to flow
(b) surface tension
(c) heat of vapourisation
(d) refractive index.

25. For the reaction, $Ag_2O_{(s)} \longrightarrow 2Ag_{(s)} + \frac{1}{2}O_{2(g)}$ which one of the following is true?
(a) $\Delta H = \Delta U$ (b) $\Delta H < \Delta U$
(c) $\Delta H > \Delta U$ (d) $\Delta H = \frac{1}{2}\Delta U$

26. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f, the entropy change is given by
(a) $\Delta S = nR \ln\left(\frac{p_f}{p_i}\right)$
(b) $\Delta S = nR \ln\left(\frac{p_i}{p_f}\right)$

(c) $\Delta S = nRT \ln\left(\frac{p_f}{p_i}\right)$

(d) $\Delta S = RT \ln\left(\frac{p_i}{p_f}\right)$ **(NEET Phase-II 2016)**

27. The specific heat of a gas at constant volume is 0.075 cal/g-K. Predict the atomicity of the gas. (Molar mass of gas is 40 g mol^{-1}.)

(a) 1 (b) 2
(c) 3 (d) None of these

28. When the temperature is increased, surface tension of water

(a) increases
(b) decreases
(c) remains constant
(d) shows irregular behaviour.

29. If an endothermic reaction occurs spontaneously at constant temperature T and pressure P, then which of the following is true?

(a) $\Delta G > 0$ (b) $\Delta H < 0$
(c) $\Delta S > 0$ (d) $\Delta S < 0$

30. 22 g solid CO_2 or dry ice is enclosed in a bottle of one litre properly closed. If temperature of bottle is raised to 25 °C to sublime all the CO_2, the pressure in bottle is

(a) 13.23 atm (b) 12.23 atm
(c) 11.23 atm (d) 14.23 atm

SOLUTIONS

1. (b) : The reaction is

$$C_6H_{6(l)} + 7\frac{1}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$$

In this reaction, O_2 is the only gaseous reactant and CO_2 is the only gaseous product.

$$\therefore \quad \Delta n_g = n_p - n_r = 6 - 7\frac{1}{2} = -\frac{3}{2}$$

Given : $\Delta U(\text{or } q_v) = -3263.9$ kJ mol^{-1}
$T = 25$ °C $= 298$ K

$$R = 8.314 \text{ J K}^{-1}\text{ mol}^{-1} = \frac{8.314}{1000} \text{ kJ K}^{-1}\text{ mol}^{-1}$$

$$\therefore \quad \Delta H\ (\text{or } q_p) = \Delta U + \Delta n_g RT$$

$$= -3263.9 - \frac{3}{2} \times \frac{8.314}{1000} \times 298$$

$$= -3263.9 - 3.7 = -3267.6 \text{ kJ mol}^{-1}$$

2. (c) : Let the number of moles of each gas $= x$

Fraction of hydrogen escaped $= \frac{1}{2}x$

$$\frac{r_{O_2}}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}} \Rightarrow \frac{n_{O_2}/t}{\frac{x}{2}/t} = \sqrt{\frac{2}{32}} = \sqrt{\frac{1}{16}} = \frac{1}{4}$$

$$\Rightarrow \frac{n_{O_2}/t}{\frac{x}{2}/t} = \frac{1}{4} \Rightarrow n_{O_2} = \frac{1}{8}x$$

Hence, fraction of oxygen escaped $= \frac{1}{8}$

3. (a) : Mass of aluminium, $m = 60.0$ g

Rise in temperature, $\Delta t = (328 \text{ K} - 308 \text{ K}) = 20$ K

Molar heat capacity, $C_m = 24$ J K^{-1} mol^{-1}

$$Q = \frac{C_m \times m \times \Delta t}{M}$$

Molar mass of Al = 27 g mol^{-1}

$$\text{Heat required} = \frac{60 \times 24 \times 20}{27} \text{ J} = 1066.7 \text{ J} \approx 1.07 \text{ kJ}$$

4. (b) : Mole fraction of C (x_C)

$$= \frac{\text{Moles of } C}{\text{Total moles in the mixture}}$$

$$= \frac{5}{2+3+5+10} = \frac{5}{20} = \frac{1}{4}$$

$\because \quad p_C = P_{total} \times x_C$

where, p_C = Partial pressure of C

$\therefore \quad P_{total} = 1.5 \times 4 = 6$ atm

5. (a) : $\Delta H = -21.976$ kcal

Here, $T_2 = 273 + 50 = 323$ K

$T_1 = 273 + 27 = 300$ K

$\Delta T = (T_2 - T_1) = (323 - 300)$ K $= 23$ K

ΔC_p = Sum of heat capacities of products – Sum of heat capacities of reactants

$= (2 \times 8.86) - [6.8 + (3 \times 6.77)]$

$= 17.72 - (6.8 + 20.31) = -9.39$ cal $degree^{-1}$

$= -9.39 \times 10^{-3}$ kcal $degree^{-1}$

Substituting these values in Kirchhoff's equation, we get

$\Delta H_2 = \Delta H_1 + (T_2 - T_1)\Delta C_p$

$= -21.976 + [23 \times (-9.39 \times 10^{-3})]$

$= -21.976 + (-0.216)$

$= -22.192$ kcal

6. (a) : Applying ideal gas equation : $pV = nRT$

For H_2 gas,

$$0.8 \times 0.5 = n_{H_2}.RT \Rightarrow n_{H_2} = \frac{0.8 \times 0.5}{RT} = \frac{0.4}{RT}$$

For O_2 gas,

$$0.7 \times 2.0 = n_{O_2}.RT \Rightarrow n_{O_2} = \frac{0.7 \times 2.0}{RT} = \frac{1.4}{RT}$$

When gas mixture is introduced in 1 L vessel, then

$p.V = (n_{H_2} + n_{O_2})RT$

$p \times 1 = \left(\frac{0.4}{RT} + \frac{1.4}{RT}\right)RT$

$\therefore \quad p = 0.4 + 1.4 = 1.8$ bar

7. (a) : $Fe_2O_{3(s)} + 3H_{2(g)} \longrightarrow 2Fe_{(s)} + 3H_2O_{(l)}$

$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_p$

$\therefore \quad \Delta C_p = \Sigma C_p$ (products) $- \Sigma C_p$ (reactants)

$= (2 \times 25.1 + 3 \times 75.3) - (103.8 + 3 \times 28.8)$

$= 276.1 - 190.2 = 85.9$ J/K $= 85.9 \times 10^{-3}$ kJ/K

$\therefore \quad \frac{\Delta H_{(358\text{ K})} - (-33.29)}{358 - 298} = 85.9 \times 10^{-3}$

$\Delta H_{358\text{ K}} = -28.14$ kJ / mol

8. (d) : Average *K.E.* for 1 mol of gas $= \frac{3}{2}RT$

Average *K.E.* for 1 molecule $= \frac{3}{2}\frac{RT}{N_A}$

9. (a) : $\Delta S_{\text{reaction}} = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}}$

$= 2 \times S_{H_2O} - [2 \times S_{H_2} + S_{O_2}]$

$= 2 \times 68 - [2 \times 126.6 + 201.20]$

$= -318.4$ J K^{-1} mol^{-1}

10. (a) : For a spontaneous reaction,

$\Delta G < 0$ *i.e.*, $\Delta H - T\Delta S < 0$

$T > \frac{\Delta H}{\Delta S}$

$T > \left(\frac{35.5 \times 1000}{83.6} = 424.6 \approx 425 \text{ K}\right)$

$\therefore \quad T > 425$ K

11. (a) : The required equation is

$CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$

Given :

(i) $C + 2S \longrightarrow CS_2$; $\quad \Delta H = 117$ kJ mol^{-1}

(ii) $C + O_2 \longrightarrow CO_2$; $\quad \Delta H = -393$ kJ mol^{-1}

(iii) $S + O_2 \longrightarrow SO_2$; $\quad \Delta H = -297$ kJ mol^{-1}

Multiplying eq. (iii) by 2 and subtract eq. (i) from it, we get

(iv) $CS_2 + 2O_2 \longrightarrow C + 2SO_2$; $\quad \Delta H = -711$ kJ mol^{-1}

Now, adding eq. (ii) and eq. (iv), we get

$CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$; $\quad \Delta H = -1104$ kJ mol^{-1}

12. (b) : For N_2 at N.T.P.,

$P = 760$ mmHg $= 101325$ N m^{-2}

$V = 22.4$ L $= 0.0224$ m^3

$M = 28$ g/mol or 0.028 kg/mol

Putting these values in the equation,

$u = \sqrt{\frac{3PV}{M}}$

$u = \sqrt{\frac{3 \times 101325 \times 0.0224}{0.028}} = 493.13$ m s^{-1}

13. (d) : For an irreversible process (work is being done by the system), $(dG)_{T,\,P} = -$ve and $(dS)_{V,\,U} = +$ve.

14. (d) : $\because \quad \frac{r_1}{r_2} = \frac{v/t_1}{v/t_2} = \sqrt{\frac{M_2}{M_1}}$

$$\frac{\frac{500\text{ mL}}{0.5\text{ h}}}{\frac{1000\text{ mL}}{t_2}} = \sqrt{\frac{M_{SO_2}}{M_{He}}} = \sqrt{\frac{64}{4}} = 4$$

Therefore, $t_2 = 4$ h

15. (c) : $q = C \times \Delta t = 30 \times 4 = 120$ kJ

Enthalpy of combustion of 4 g of graphite $= -120$ kJ

Enthalpy of combustion of 1 mole of graphite

$= -\frac{12}{4} \times 120 = -360$ kJ mol^{-1}

16. (c) : $c_{rms} = \sqrt{\frac{3RT}{M}}$

$\frac{c_{rms(H_2)}}{c_{rms(N_2)}} = \sqrt{\frac{T_{(H_2)}}{M_{(H_2)}} \times \frac{M_{(N_2)}}{T_{(N_2)}}}$

$\sqrt{7} = \sqrt{\frac{T_{(H_2)}}{T_{(N_2)}} \times \frac{28}{2}} \Rightarrow \frac{T_{(H_2)}}{T_{(N_2)}} = \frac{1}{2}$

$2T_{(H_2)} = T_{(N_2)}$

$\therefore \quad T_{(H_2)} < T_{(N_2)}$

17. (b) : Real gases show ideal behaviour at high temperature and low pressure.

18. (d) : Volume of 0.0168 mol of O_2 at STP

$= 0.0168 \times 22400$ mL $= 376.3$ mL

$V_1 = 376.3$ mL, $P_1 = 760$ mmHg, $T_1 = 273$ K

$V_2 = 428$ mL, $P_2 = ?$, $T_2 = 298$ K

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{760 \times 376.3}{273} = \frac{P_2 \times 428}{298}$

$\Rightarrow \quad P_2 = 729.4$ mmHg

$\therefore \quad$ Pressure of water vapour $= 754 - 729.4$

$= 24.6$ mmHg

19. (c)

20. (c) : $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \Rightarrow p_2 = \frac{p_1V_1T_2}{T_1V_2}$ ...(i)

Substituting values in eq. (i),

$$p_2 = (0.75 \text{ N m}^{-2}) \frac{V_1}{(3V_1)} \frac{(2T_1)}{T_1}$$

$p_2 = 0.5 \text{ N m}^{-2}$

21. (a) : The entropy change at the melting point of a substance is given by

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_{\text{melting}}}$$

$$\therefore \quad T_{\text{melting}} = \frac{\Delta H_{fus}}{\Delta S_{fus}}$$

$$= \frac{7.25 \text{ kJ mol}^{-1}}{0.007 \text{ kJ K}^{-1} \text{ mol}^{-1}} = 1035.7 \text{ K}$$

Hence, the melting point of KCl is 1035.7 K

22. (a) : $\overset{*}{c} : \bar{c} : c = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1 : 1.128 : 1.224$$

23. (d) **24. (b)**

25. (c) : $\Delta H = \Delta U + \Delta n_g RT$

$$\because \quad \Delta n_g = \frac{1}{2} - 0 = \frac{1}{2}$$

$$\therefore \quad \Delta H = \Delta U + \frac{1}{2} RT$$

$$\therefore \quad \Delta H > \Delta U$$

26. (b) : For an ideal gas undergoing reversible expansion, when temperature changes from T_i to T_f and pressure changes from p_i to p_f,

$$\Delta S = nC_p \ln \frac{T_f}{T_i} + nR \ln \frac{p_i}{p_f}$$

For an isothermal process, $T_i = T_f$ so, $\ln 1 = 0$

$$\therefore \quad \Delta S = nR \ln \frac{p_i}{p_f}$$

27. (a) : $C_v = 0.075 \times 40 = 3 \text{ cal K}^{-1} \text{ mol}^{-1}$

$C_p - C_v = = R$

$\Rightarrow \quad C_p - 3 = 2 \quad \Rightarrow \quad C_p = 5 \text{ cal K}^{-1} \text{ mol}^{-1}$

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.66$$

Thus, the gas is monoatomic.

28. (b) : The decrease in surface tension with increase in temperature is due to the fact that with the increase in temperature, the kinetic energy of the molecules increases and hence, the intermolecular attraction between the molecule decreases.

29. (c) : $\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$\Delta S > 0$, for spontaneous process.

30. (a) : $w = 22$ g; $V = 1$ litre, $T = 298$ K

$$PV = \frac{w}{M} RT \quad (\text{Molar mass of } CO_2 = 44 \text{ g mol}^{-1})$$

$$P_{CO_2} \times 1 = \frac{22}{44} \times 0.0821 \times 298$$

$$\therefore \quad P_{CO_2} = 12.23 \text{ atm}$$

$$\therefore \quad P_{\text{in bottle}} = P_{CO_2} + P_{\text{atm}}$$

$$= 12.23 + 1 = 13.23 \text{ atm}$$

EXAMiNER'S MiND CLASS XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

CHEMICAL BONDING AND MOLECULAR STRUCTURE

SECTION - I

Only One Option Correct Type

1. Which of the following has highest bond angle?
(a) NO_2^+ (b) NO_2 (c) NO_2^- (d) NO_3^-

2. In PO_4^{3-} ion, the formal charge on the oxygen atom of P—O bond is
(a) +1 (b) −1 (c) −0.75 (d) +0.75

3. The ionic bond A^+B^- is formed when
(1) *I.E.* of *A* is low (2) *E.A.* of *B* is high
(3) lattice energy of *AB* is high
(4) lattice energy of *AB* is low.
(a) 1 and 2 (b) 1, 2 and 3
(c) 3 only (d) 4 only

4. Which of the following compounds/ions has V-shape?
(a) SF_5^- (b) SF_4 (c) OSF_4 (d) SF_2

5. In which one of the following species the central atom has the type of hybridisation which is not the same as in the other three?
(a) $SbCl_5^{2-}$ (b) PCl_5 (c) SF_4 (d) I_3^-

6. The correct increasing order of *s*-character (in percentage) in the hybrid orbitals in the given molecules/ions is (assume all hybrid orbitals are exactly equivalent) :

CO_3^{2-}	XeF_4	I_3^-	NCl_3	$BeCl_2$
I	II	III	IV	V

(a) II < III < IV < I < V (b) II < IV < III < V < I
(c) III < II < I < V < IV (d) II < IV < III < I < V

7. In ICl_2^+, ICl_2^-, and ICl_4^-, sum of the bond pairs and lone pairs on each iodine atom are respectively
(a) 2, 2 and 4 (b) 2, 3 and 2
(c) 4, 5 and 4 (d) 4, 5 and 6

8. Which of the following molecules is formed by *p-p* overlapping?
(a) F_2 (b) H_2O (c) HCl (d) NH_3

9. In XeF_2 molecule, the angle between two lone pair orbitals is α, the angle between lone pair orbital and bond pair orbital is β and the angle between two bond pair orbitals is γ then, which one is correct order of angle?
(a) $\alpha = \beta = \gamma$ (b) $\alpha > \beta > \gamma$
(c) $\gamma > \beta > \alpha$ (d) $\gamma > \alpha > \beta$

10. Which one of the following properties is not shown by NO?
(a) Its bond order is 2.5.
(b) It is diamagnetic in gaseous state.
(c) It is a neutral oxide.
(d) It combines with oxygen to form nitrogen dioxide.

SECTION - II

More than One Options Correct Type

11. According to VBT in XeF_2, Xe uses five sp^3d hybridised orbital for molecule formation. Select correct statement for XeF_2.
(a) Three sp^3d orbitals are used for covalent bonding with F.
(b) Three sp^3d orbitals occupy lone pairs of Xe.
(c) Two sp^3d orbitals are used for covalent bonding with F.
(d) Two sp^3d orbitals are occupied by lone pairs of Xe.

12. Which statements are correct for AB_x type molecule?
(a) If the electronegativity of central atom decreases, the bond angle decreases.
(b) If the size of central atom increases, the bond angle decreases.
(c) If the electronegativity of atom B decreases, the bond angle increases.
(d) If the electronegativity of atom B decreases, the bond angle decreases.

13. Which of the following statements are not correct?
(a) Hybrid orbitals form stronger bonds than p-orbitals.
(b) Excitation of electron is essential for hybridisation.
(c) Boiling point of H_2O is more than H_2S.
(d) Resonance plays an important role in molecular orbital theory.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

Hydrogen bonding originates from the dipole-dipole interaction between H-atom and any of the other atom like F, O, N and in some cases with Cl atom also. There are two types of H-bonding *i.e.*; intermolecular and intramolecular H-bonding.

14. Which of the following molecules does not consist of intramolecular H-bonding?
(a) Chloral
(b) Chloral hydrate
(c) *o*-Hydroxybenzaldehyde
(d) *o*-Chlorophenol

15. Which of the following statements is incorrect?
(a) Boiling point of H_2O_2 is greater than that of H_2O.
(b) Ethylene glycol is less viscous than glycerol.
(c) *o*-Nitrophenol can be separated from its *m*- and *p*-isomers using its steam volatile property.
(d) In ice, each 'O' atom is tetrahedrally arranged by four H-atoms which are all equidistant.

Paragraph for Questions 16 and 17

The VSEPR model considers double and triple bonds to have slightly greater repulsive effects than single bonds because of the repulsive effect of π-electrons. Consider molecule $(CH_3)_2C=CH_2$ for given questions :

16. Which type of overlapping is not observed in the given molecule?
(a) sp^3-s (b) sp^2-s
(c) $sp-s$ (d) sp^2-sp^2

17. Select which has the largest bond angle in the given molecule.
(a) CH_3-C-CH_3 (b) $H_3C-C=C$
(c) $H-C-H$ (d) All are same.

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I (Species)		List II (Properties)
A.	O_2^{2-}	P.	Isoelectronic with N_2
B.	CO	Q.	Fractional bond order
C.	NO^+	R.	Paramagnetic
D.	He_2^+	S.	Diamagnetic

	A	B	C	D
(a)	P	R, S	Q, P	P, S
(b)	Q, P	S	P, S	R, S
(c)	S	P, S	P, S	Q, R
(d)	R	R, S	S	P, Q

19. Match the List I with List II and select the correct answer using the codes given below the lists :

List I	List II
(P) CH_4	1. Linear molecule
(Q) $BeCl_2$	2. Tetrahedral molecule
(R) H_2O	3. Pyramidal molecule
(S) NH_3	4. V-shaped molecule

	P	Q	R	S
(a)	2	1	4	3
(b)	2	3	4	1
(c)	1	2	3	4
(d)	2	3	1	4

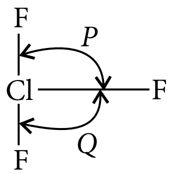
SECTION - V

Assertion Reason Type

20. **Assertion :** C_2H_2 molecule is linear.
Reason : In C_2H_2, carbon atoms remain unhybridised.

21. **Assertion :** H_2 molecule is more stable than HeH molecule.
Reason : The antibonding electron in the molecule destabilises HeH.

22. **Assertion :** In ClF_3 molecule,



$P = Q \neq 90°$

Reason : The molecule is slightly bent T-shaped and there is repulsion between lone pairs of electrons.

SECTION - VI

Integer Value Correct Type

23. How many of the following compounds violate octet rule?
BrF_5, SF_6, IF_7, $XeOF_4$, ClF_2^-, PCl_4^+

24. A diatomic molecule has a dipole moment of 1.2 D. If the bond distance is 1.0 Å, $1/x$ of an electronic charge 'e' exists on each atom. The value of x is

25. The number of dative bonds in sulphuric acid molecule is

HYDROGEN

SECTION - I

Only One Option Correct Type

1. Which one of the following processes will produce permanent hard water?
(a) Addition of Na_2SO_4 to water
(b) Saturation of water with $CaCO_3$
(c) Saturation of water with $MgCO_3$
(d) Saturation of water with $CaSO_4$

2. Reaction between following pairs will produce hydrogen except
(a) Cu + HCl (b) Fe + $H_2O_{(steam)}$
(c) Mg + H_2O (hot) (d) Na + Alcohol.

3. Protium, deuterium, tritium differ in
(a) number of protons and physical properties
(b) atomic number and chemical properties
(c) number of neutrons and physical properties
(d) number of neutrons and chemical properties.

4. Moist hydrogen peroxide cannot be dried over conc. H_2SO_4 because
(a) it is oxidised by H_2SO_4
(b) it is reduced by H_2SO_4
(c) it can catch fire
(d) all of these.

5. Which of the following equations depicts reducing nature of H_2O_2?
(a) $2[Fe(CN)_6]^{4-} + 2H^+ + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$
(b) $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$
(c) $Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$
(d) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

6. Heavy water is manufactured
(a) by repeated electrolysis of water with 3% aqueous NaOH
(b) by electrolysis of water containing heavy hydrogen dissolved in it
(c) by combination of hydrogen and heavier isotope of oxygen
(d) none of the above.

7. Which of the following explanations justifies for not placing hydrogen in either the group of alkali metals or halogens?
(a) Hydrogen is much lighter than alkali metals or halogens.
(b) Hydrogen atom does not contain any neutron.
(c) The ionization energy of hydrogen is too high for group of alkali metals and too low for halogen group.
(d) Hydrogen can form compounds with almost all other elements.

8. The freezing point of heavy water is
(a) –3.82°C (b) 3.82°C
(c) 0°C (d) – 10°C

9. Water softening by Clark's process involves use of
(a) calcium carbonate (b) sodium carbonate
(c) potash alum (d) calcium hydroxide.

10. Which is false about H_2O_2?
(a) It can act as both oxidising and reducing agent.
(b) Two —OH bonds lie in the same plane.
(c) It is pale blue liquid.
(d) It can be oxidised by O_3.

SECTION - II

More than One Options Correct Type

11. Which of the following statements are correct?
(a) Metallic hydrides are deficient of hydrogen.
(b) Metallic hydrides conduct heat and electricity.
(c) Ionic hydrides do not conduct electricity in solid state.
(d) Ionic hydrides are very good conductors of electricity in solid state.

12. Which of the following statements are correct?
(a) Dissociation of H_2 molecules is an endothermic process.
(b) Hydrogen at the moment of liberation is more active.
(c) Atomic hydrogen is powerful reducing agent.
(d) Ordinary hydrogen is an oxidising agent.

13. Which of the following statements are correct about 6.8% strength of H_2O_2?
(a) Its normality is 4 N.
(b) Its molarity is 2 M.
(c) Its volume strength is 22.4 V.
(d) Volume strength = 11.2 × *M*.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

Hydrogen peroxide is a powerful oxidising agent, both in the acidic and alkaline medium.

In acidic medium; $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$

In alkaline medium; $H_2O_2 + 2e^- \longrightarrow 2OH^-$

Hydrogen peroxide acts as a reducing agent towards powerful oxidising agents.

In acidic medium; $H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$

In alkaline medium, however, its reducing nature is more effective.

$$H_2O_2 + 2OH^- \longrightarrow 2H_2O + O_2 + 2e^-$$

14. On addition of H_2O_2 to acidified $KMnO_4$, $KMnO_4$ gets decolourised due to
(a) oxidation of $KMnO_4$
(b) reduction of $KMnO_4$
(c) both oxidation and reduction
(d) none of these.

15. In which of the following reactions, H_2O_2 acts as an oxidising agent?
(a) $2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$
(b) $IO_4^- + H_2O_2 \longrightarrow IO_3^- + H_2O + O_2$
(c) $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$
(d) $2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

Paragraph for Questions 16 and 17

Formation of methane from syn gas is represented by the following equations :

(i) $C + H_2O \longrightarrow \underbrace{CO + H_2}_{\text{syn gas}}$

(ii) $\underbrace{CO + H_2}_{\text{syn gas}} + X \xrightarrow{\text{Catalyst}} CO_2 + 2H_2$

(iii) $CO + 3H_2 \xrightarrow{\text{Ni}} CH_4 + H_2O$

16. *X* in reaction (ii) refers to
(a) liquid water
(b) steam
(c) oxygen
(d) carbon monoxide.

17. Hydrogen prepared by above method is passed over Ni catalyst
(a) to remove traces of CO
(b) to prepare H_2O
(c) to prepare CH_4
(d) to separate H_2 from water gas.

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I		List II
(P)	Synthesis gas	1.	Forms stoichiometric compounds with *s*-block elements
(Q)	Dihydrogen	2.	Prolonged electrolysis of water
(R)	Heavy water	3.	Mixture of CO and H_2
(S)	Hydrogen peroxide	4.	Zn + NaOH
		5.	Oxidising agent and/or Reducing agent

	P	Q	R	S
(a)	1, 2	3	4, 5	1, 2
(b)	3	1, 4, 5	2	5
(c)	1, 2	3, 4	1, 5	4
(d)	1, 3	2, 3	4	5

19. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I		List II
(P)	Ionic hydride	1.	LiH
(Q)	Electron deficient hydride	2.	CaH_2
(R)	Hydrolith	3.	AlH_3
(S)	Covalent hydride	4.	SiH_4

	P	Q	R	S
(a)	1	2,3	3	1, 4
(b)	2,3	1	2	1, 4
(c)	1, 2	3	2	3, 4
(d)	3,4	3	2	1, 2

SECTION - V

Assertion Reason Type

20. **Assertion :** *Para*-hydrogen with lower energy is favoured at high temperature.
Reason : The thermal conductivity of *para*-hydrogen is lesser than that of *ortho*-hydrogen.

21. **Assertion :** Permanent hardness of water is removed by treatment with washing soda.
Reason : Washing soda reacts with soluble magnesium and calcium sulphates to form insoluble carbonates.

22. **Assertion :** The colour of old lead paintings can be restored by washing with dilute solution of H_2O_2.
Reason : Black lead sulphide is oxidised by H_2O_2 to white lead sulphate.

SECTION - VI

Integer Value Correct Type

23. Half litre each of three samples of H_2O_2 labelled 10 vol, 15 vol, 20 vol are mixed and then diluted with 1700 mL of water. Calculate relative strength of resultant H_2O_2 solution.

24. Calculate the degree of hardness of a sample of water containing 6 mg of $MgSO_4$ per kg of water.

25. What is the sum of protons, electrons and neutrons in the heaviest isotope of hydrogen?

SOLUTIONS

CHEMICAL BONDING AND MOLECULAR STRUCTURE

1. **(a) :** NO_2^+ has linear geometry and therefore, bond angle is highest (180°).

2. **(c) :** In PO_4^{3-} ion, formal charge on each O-atom of P—O bond

$$= \frac{\text{Total charge}}{\text{Number of O-atoms}} = -\frac{3}{4} = -0.75$$

3. **(b)**

4. **(d) :** SF_2 has sp^3 hybridisation and 'V' shape due to the presence of two lone pairs on sulphur.

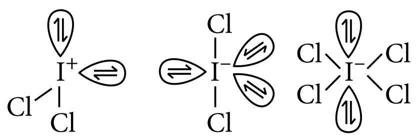
5. **(a) :** $SbCl_5^{2-}$ has sp^3d^2 hybridisation while all other species involve sp^3d hybridisation.

6. **(a) :**

Species	Hybridisation
CO_3^{2-}	sp^2
XeF_4	sp^3d^2
I_3^-	sp^3d
NCl_3	sp^3
$BeCl_2$	sp

Therefore, the correct increasing order of percentage of *s*-character is :
II < III < IV < I < V

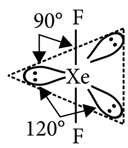
7. **(d) :**



So, total number of lone pairs and bond pairs
in $ICl_2^+ = 2 + 2 = 4$
in $ICl_2^- = 3 + 2 = 5$ and $ICl_4^- = 2 + 4 = 6$

8. **(a) :** F_2 is formed by *p*-*p* overlapping whereas, H_2O, HCl and NH_3 are formed by *s*-*p* overlapping.

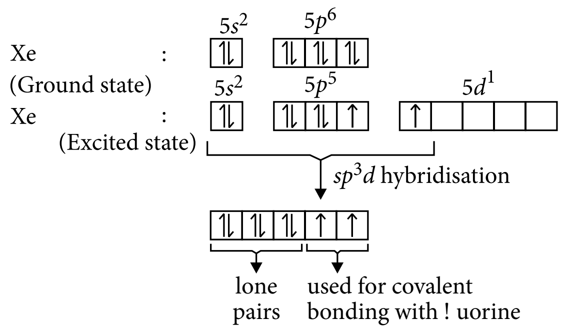
9. **(d) :**



$\alpha = 120°$
$\beta = 90°$
$\gamma = 180°$
$\gamma > \alpha > \beta$

10. **(b) :** NO is paramagnetic in gaseous state due to the presence of one unpaired electron.

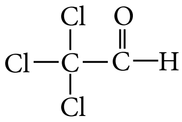
11. **(b,c) :**



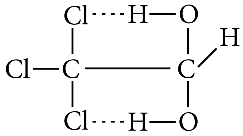
12. **(a, b, c)**

13. **(b, d) :** Excitation of electron is not essential for hybridisation, vacant orbitals can also participate in hybridisation. Resonance has no role in M.O. theory.

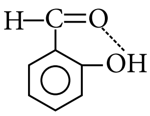
14. (a)

(a) 

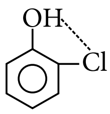
Chloral

(b) 

Chloral hydrate

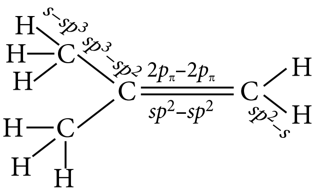
(c) 

o-Hydroxy benzaldehyde

(d) 

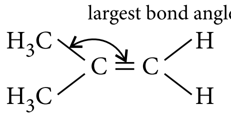
o-Chlorophenol

15. (d)

16. (c) : 

There is no *sp–s* overlapping.

17. (b): largest bond angle



18. (c) : $O_2^{2-}(18):\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z^2, \pi 2p_x^2$
$= \pi 2p_y^2, \pi^*2p_x^2 = \pi^*2p_y^2$

Diamagnetic

$$\text{B.O.} = \frac{N_b - N_a}{2} = \frac{10-8}{2} = 1$$

$N_2 = CO = NO^+ = 14e^-$

CO and $NO^+ : \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \pi 2p_x^2$
$= \pi 2p_y^2, \sigma 2p_z^2$

Diamagnetic

$$\text{B.O.} = \frac{10-4}{2} = 3$$

$He_2^+(3) : \sigma 1s^2 \sigma^*1s^1$

Paramagnetic

$$\text{B.O.} = \frac{2-1}{2} = \frac{1}{2}$$

19. (a) : (P) $\rightarrow$ 2 : CH_4 is sp^3 hybridised so, it is tetrahedral molecule.

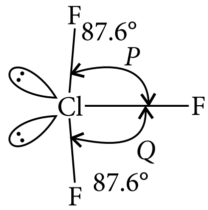
(Q) $\rightarrow$ 1 : $BeCl_2$ is *sp* hybridised, hence linear in shape.

(R) $\rightarrow$ 4 : H_2O is sp^3 hybridised, but due to the presence of the lone pairs, it is V-shaped.

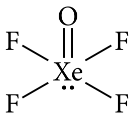
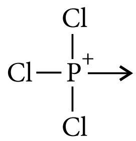
(S) $\rightarrow$ 3 : NH_3 is sp^3 hybridised, but due to the presence of one lone pair of electrons, its shape is pyramidal.

20. (c) : In C_2H_2, C atom is *sp*-hybridised. Thus, linear in shape.

21. (a) : Bond order of H_2 = 1 (2 electrons; $\sigma 1s^2$).
Bond order of HeH = 0.5 (3 electrons, $\sigma 1s^2$, σ^*1s^1).
Greater the bond order of molecule, more stable the molecule. Hence, H_2 is more stable than HeH.

22. (a) : 

due to *lp* – *lp* repulsion

23. (5) : (i) BrF_5 = 12 electrons
(ii) SF_6 = 12 electrons
(iii) IF_7 = 14 electrons
(iv) $XeOF_4$;  = 14 electrons
(v) ClF_2^- ; $[F—\ddot{Cl}—F]^-$ = 10 electrons
(vi) PCl_4^+ ;  Cl = 8 electrons

Hence, except PCl_4^+ all five molecules violate octet rule.

24. (4) : Partial charge = $\dfrac{\text{Dipole moment}}{\text{Bond distance}}$

$$= \frac{1.2 \times 10^{-18}\,\text{esu.cm}}{1.0 \times 10^{-8}\,\text{cm}} = 1.2 \times 10^{-10}\ \text{esu}$$

The fraction of an electronic charge is

$$\frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} = \frac{1}{4} \quad \therefore \quad \text{Value of } x = 4$$

25. (2)

HYDROGEN

1. (d): Permanent hardness of water is due to the presence of soluble chlorides and sulphates of calcium and magnesium.

2. (a) : (a) Cu + HCl $\longrightarrow$ No reaction
(b) $\underset{\text{Steam}}{3Fe + 4H_2O} \longrightarrow \underset{\text{Ferroso ferric oxide}}{Fe_3O_4} + 4H_2$

(c) $Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$
(d) $2Na + 2C_2H_5OH \longrightarrow 2C_2H_5ONa + H_2$

3. (c)

4. (a): H_2SO_4 acts as an oxidising agent and decomposes H_2O_2.
$H_2O_2 + [O] \longrightarrow H_2O + O_2$

5. (b): When H_2O_2 behaves as a reducing agent, it evolves molecular oxygen during the reaction. Therefore, only in option (b), it behaves as a reducing agent.

6. (a): Heavy water is manufactured by repeated electrolysis of water (containing a little NaOH).

7. (c): Hydrogen has ionization energy value which is too high as compared to alkali metals and too low as compared to halogens and thus, cannot be placed in any of these two groups.

8. (b) **9. (d)**

10. (b): The two O–H bonds are in different planes due to repulsion between different bonding and antibonding orbitals.

11. (a, b, c)

12. (a, b, c): Compounds which undergo reduction on heating with H_2 are reduced by atomic H at ordinary temperature.

$$H_2 \xrightarrow[\text{Low pressure, 2273 K}]{\text{Electric arc}} H + H - \text{Heat}$$

The H so produced is very reactive and its life is only one-third of a second.

13. (a, b, c, d):

$$\text{Volume strength} = 5.6 \times \frac{\text{Percentage strength}}{\text{eq. wt. of } H_2O_2} \times 10$$

$$= 5.6 \times \frac{6.8}{17} \times 10 = 22.4 \text{ V}$$

(a) $\text{Normality} = \dfrac{\text{Volume strength}}{5.6} = 4 \text{ N}$

(b) $\text{Molarity} = \dfrac{\text{Volume strength}}{11.2} = 2 \text{ M}$

(c) Volume strength = 22.4 V

(d) Volume strength = 11.2 × molarity = 22.4 V

14. (b): $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$5H_2O_2 + 5[O] \longrightarrow 5H_2O + 5O_2$

$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

On the other hand, we can write it as,

$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

15. (a): $2I^- \longrightarrow I_2$, hence H_2O_2 acts as an oxidising agent.

16. (b): Water gas is mixed with steam, producing CO_2.

17. (a): The hydrogen manufactured by the given method is utilised for synthesis of NH_3 in which CO acts as a poison for catalyst. Thus, Ni is used to remove traces of CO.

18. (b) **19. (c)**

20. (d): *Para*-hydrogen with lower energy is favoured at low temperature.
The thermal conductivity of *para*-hydrogen is 50% greater than that of *ortho*-hydrogen.

21. (a) **22. (a)**

23. (7): Volume strength of $H_2O_2 = 5.6 \times N$

$$10 \text{ vol. } H_2O_2 = \frac{10}{5.6} \text{ N } H_2O_2$$

$$15 \text{ vol. } H_2O_2 = \frac{15}{5.6} \text{ N } H_2O_2$$

$$20 \text{ vol. } H_2O_2 = \frac{20}{5.6} \text{ N } H_2O_2$$

As 500 mL of each is mixed then total volume of mixture = 1500 mL
Also this is diluted with 1700 mL, so total volume becomes 3200 mL

$$N \times 3200 = \frac{10 \times 500}{5.6} + \frac{15 \times 500}{5.6} + \frac{20 \times 500}{5.6}$$

$$\text{or } N_{H_2O_2} = \frac{500 \times 45}{5.6 \times 3200} = 1.255 \text{ N}$$

$\therefore$ Volume strength of $H_2O_2 = 1.255 \times 5.6 = 7.03 \approx 7$

24. (5): 1 g-mole or 120 g $MgSO_4 \equiv$ 1 g-mole or 100 g $CaCO_3$

$$6 \times 10^{-3} \text{ g } MgSO_4 = \frac{100 \times 6 \times 10^{-3}}{120}$$

$$= 5 \times 10^{-3} \text{ g of } CaCO_3$$

Thus, 1000 g of water contains $MgSO_4$ equivalent to

$$5 \times 10^{-3} \text{ g of } CaCO_3 = \frac{5 \times 10^{-3}}{1000} \times 10^6$$

10^6 g of water will contain = 5 g of $CaCO_3$

$\therefore$ Hardness of given water sample = 5 ppm

25. (4): Tritium T or ${}^3_1H$, the heaviest isotope of hydrogen has 1 proton, 2 neutrons and 1 electron. Hence, sum of protons, neutrons and electrons is 4.

◈◈

ACE YOUR WAY CBSE XI

Series 3

CHAPTERWISE PRACTICE PAPER : STATES OF MATTER | THERMODYNAMICS

Time Allowed : 3 hours | Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Under what conditions q and w become state functions?

2. What would have happened to the gas if the molecular collisions were not elastic?

3. The C_p and C_v of a gas are 20.834 and 12.520 J K^{-1} mol^{-1} respectively. What is the atomicity of the gas?

4. How is the mole fraction of a gas component related to its partial pressure and the total pressure?

5. What is residual entropy?

6. Acetic acid (ethanoic acid) and hydrochloric acid react with KOH solution. The enthalpy of neutralisation of ethanoic acid is –55.8 kJ mol^{-1} while that of hydrochloric acid is –57.1 kJ mol^{-1}. Why are these two values different?

7. **(a)** Why does sharp glass edge become smooth on heating it upto its melting point in a flame? Explain which property of liquids is responsible for this phenomenon.
(b) Which two other properties of liquids can be explained on the basis of the above property?

8. Distinguish between the total kinetic energy of a molecule and its translational kinetic energy. For what type of gas molecules these two are same?

9. **(a)** Define Charles' law.
(b) What is the coefficient of volume expansion of a gas?

10. What do you understand by the term 'absolute zero temperature'? What is its significance?

OR

How does the magnitude of the enthalpy change depend on the strength of the intermolecular interaction for the substances undergoing phase changes? Explain with example.

11. Which of the following processes are accompanied by an increase of entropy?
(a) Dissolution of iodine in a solvent.
(b) HCl is added to $AgNO_3$ solution and precipitate of AgCl is obtained.
(c) A partition is removed to allow the gases to mix.

12. 20% of N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Calculate the density of the equilibrium mixture.

13. Calculate the standard Gibbs energy change for the formation of propane at 298 K.

$3C_{(graphite)} + 4H_{2(g)} \rightarrow C_3H_{8(g)}$

$\Delta_f H°$ for propane, $C_3H_{8(g)} = -103.8$ kJ mol^{-1}

(Given : $S°_m$ $[C_3H_{8(g)}] = 270.2$ J K^{-1} mol^{-1}

$S°_{m\ (graphite)} = 5.70$ J K^{-1} mol^{-1}

and $S°_m$ $[H_{2(g)}] = 130.7$ J K^{-1} mol^{-1})

14. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

15. 1 Litre flask containing $NH_{3(g)}$ at 2.0 atm at 200 K is connected by a narrow tube of negligible volume to another 800 mL flask containing $HCl_{(g)}$ at 8.0 atm at 200 K. The two gases react according to equation :

$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$; $\Delta H = -43$ kJ/mol

If heat capacity of $HCl_{(g)}$ is 20 J K^{-1} mol^{-1}, determine the heat produced, final temperature and final pressure inside the flask. (The heat capacity of flask and volume of solid NH_4Cl in flask is negligible.)

16. (a) (i) How many calories are required to heat 100 g of copper (s = 0.092 cal/g/K) from 10 to 100°C?

(ii) The same quantity of heat as in (i) is added to 100 g of aluminium (s = 0.217 cal/g/K) at 10°C. Which gets hotter, the copper or aluminium?

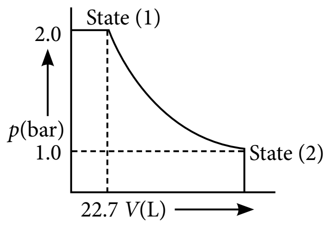
(b) How much heat is required to change 10 g ice at 0°C to steam at 100°C ? Latent heat of fusion and vaporization for H_2O are 80 cal/g and 540 cal/g respectively. Specific heat of water is 1 cal/g.

17. A student forgot to add the reaction mixture to the round bottom flask at 27°C but put it on the flame. After a lapse of time, he realised his mistake, using a pyrometer he found the temperature of the flask was 477°C. What fraction of air would have been expelled out?

OR

The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20°C and one bar will be released when 0.15 g of aluminium reacts?

18. (a) 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in figure. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.



(b) A certain volume of dry air at NTP is expanded reversibly to four times its volume isothermally. Calculate the final pressure.

19. A sample of 0.16 g CH_4 was subjected to combustion at 27°C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume and (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K^{-1} and R is 8.314 J K^{-1} mol^{-1}.

20. Give reasons for the following :

(a) The size of balloon becomes larger and larger as it ascends into higher altitudes.

(b) Tyres of automobiles are inflated to lesser pressure in summer than in winter.

21. Calculate the rise in temperature when a gas, for which $\gamma = 1.5$, is compressed to 27 times its original pressure, assuming the initial temperature to be 27°C.

22. (a) Calculate the maximum efficiency of an engine operating between 100°C and 25°C.

(b) Same mass of diamond and graphite (both being carbon) are burnt in oxygen. Will the heat produced be same or different? Why?

23. Sejal asked Saloni that why people are undergoing medical check up before going on Amarnath Yatra. Saloni explained the reason to Sejal and Sejal got satisfied, meanwhile Rishabh told that liquid boils at lower temperature at a hill station than in a plane area.

(a) What reason was explained by Saloni to satisfy Sejal?

(b) Why does liquid boil at lower temperature at hills stations?

(c) What values are associated with Saloni?

(d) What is critical temperature?

24. Nitrogen molecule (N_2) has radius of about 0.2 nm. Assuming that nitrogen molecule is spherical in shape, calculate

(a) volume of a single molecule of N_2.

(b) the percentage of empty space in one mole of N_2 gas at S.T.P.

OR

(a) When an ideal gas expands in vacuum, there is neither absorption nor evolution of heat. Why?

(b) Determine the value of ΔH and ΔU for the reversible isothermal evaporation of 90.0 g of water at 100°C. Assume that water behaves as an ideal gas and heat of evaporation of water is 540 cal g^{-1}.

25. The density of the vapours of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3}. The vapours effuse through a small hole at a rate of 1.33 times faster than oxygen under the same conditions :

(a) Determine : (i) molecular weight, (ii) molar volume, (iii) compressibility factor (Z) of the vapours, (iv) Which forces among gas molecules are dominating, the attractive or the repulsive?

(b) If the vapours behave ideally at 1000 K, determine the average translational kinetic energy of a molecule.

OR

Two moles of a perfect gas undergo the following process :

(a) A reversible isobaric expansion from (1 atm, 20 L) to (1 atm, 40 L).

(b) A reversible isochoric change of state from (1 atm, 40 L) to (0.5 atm, 40 L).

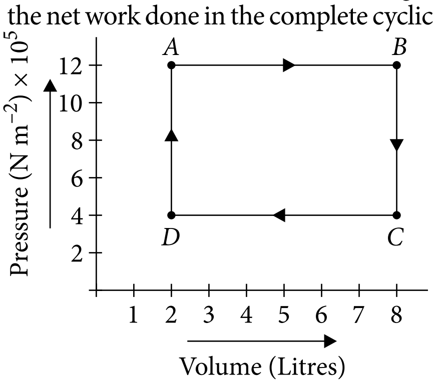
(c) A reversible isothermal compression from (0.5 atm, 40 L) to (1 atm, 20 L).

(i) Sketch with labels each of the process on the same P–V diagram.

(ii) Calculate the total work (w) and the total heat change (q) involved in the above process.

(iii) What will be the values of ΔU, ΔH and ΔS for the overall process?

26. (a) The figure given below represents P–V diagrams of different stages of a thermodynamic process. Calculate the work done in each stage and also the net work done in the complete cyclic process.



(b) Give a statement which includes the main ideas of the first law and second law of thermodynamics.

OR

(a) The composition of the equilibrium mixture ($Cl_2 \rightleftharpoons 2Cl$), which is attained at 1200°C, is determined by measuring the rate of effusion through a pin hole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms (atomic weight of Kr is 84).

(b) The compression factor (compressibility factor) for 1 mol of a van der Waals' gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals' constant a.

SOLUTIONS

1. In a thermodynamically reversible process.

2. On every collision, there would have been loss of energy. As a result, the molecules would have slowed down and ultimately settle down. The gas pressure would have gradually become zero.

3. $\gamma = \dfrac{C_p}{C_v} = \dfrac{20.834}{12.520} = 1.66$

Therefore, the gas is monoatomic.

4. Mole fraction, is equal to the partial pressure divided by the total pressure.

$$x_i = \frac{p_i}{P_{\text{total}}}$$

5. The entropy possessed by a substance at absolute zero is called residual entropy.

6. Ethanoic acid is a weak acid while hydrochloric acid is strong acid (completely ionized). The enthalpy of neutralisation of weak acid (ethanoic acid) and strong base (KOH) is numerically less than – 57.1 kJ mol^{-1} (heat of neutralisation of strong acid and strong base) because the ionization of ethanoic acid is not complete in solution and some energy is utilised for dissociating acid molecules.

7. **(a)** On heating the glass, it melts and takes up rounded shape at the edges which has minimum surface area. This is due to the property of surface tension of liquids.

(b) The following two properties of liquids can be explained on the basis of surface tension :

(i) Capillary action of water.

(ii) Spherical shape of small droplets.

8. The total kinetic energy of a molecule includes the translational kinetic energy, rotational kinetic energy and vibrational kinetic energy.
For monoatomic gases, both rotational and vibrational kinetic energies are zero. Therefore, for these gases, total kinetic energy is equal to translational kinetic energy.

9. **(a)** Charles' law states that "The volume of a given amount of a gas at constant pressure varies directly with its absolute temperature.
$V \propto T$ (pressure is constant)
(b) According to Charles' law,

$$V_t = V_0\left(1+\frac{t}{273}\right) = V_0\,(1+\alpha t)$$

$$\alpha = \frac{\;}{273} = \text{Coefficient of volume expansion}$$

here, V_0 = Volume at 0°C and V_t = Volume at t°C

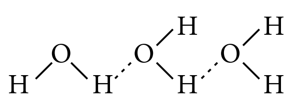
10. According to Charles' law, if a gas is cooled to –273°C, its volume becomes zero as

$$\text{Volume at } -273°\text{C} = V_0\left(1-\frac{273}{273}\right) = 0$$

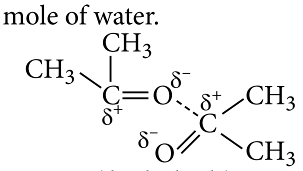
where, V_0 = Volume at 0°C
This means that –273°C should be the lowest temperature because any further cooling would lead to a volume less than zero or negative volume which is meaningless. Therefore, this temperature is termed as absolute zero temperature. But volume never approaches zero at –273°C because all gases condense to liquid or solid before the attainment of this temperature.

OR

The magnitude of the enthalpy change depends directly on the strength of the intermolecular interaction.
For example, intermolecular hydrogen bonding between water molecules lead to large attractive intermolecular energy holding water molecules tightly in liquid phase. For an organic liquid such as acetone, the intermolecular dipole-dipole interactions are significantly weaker. Thus, it requires less heat to vaporise 1 mole of acetone than it does to vaporise one mole of water.



(H-bonding)



(dipole-dipole)

11. **(a)** Entropy is increased because solid iodine is converted into liquid phase (solution).
Order of entropy : Gases > liquids > solids
(b) $HCl + AgNO_3 \rightarrow AgCl\downarrow + HNO_3$
In this reaction, liquid HCl is mixed with the solution of $AgNO_3$ and the formation of AgCl(ppt.) occurs, hence entropy is decreased.
(c) Entropy is increased because after removing the partition both the gases will mix and move upto larger space, thus the randomness of the molecules will increase.

12.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
At $t = 0$	1 mol		0
At equilibrium	(1 – 0.2) mol		0.4

Total moles = 0.8 + 0.4 = 1.2
$PV = nRT$
$1 \times V = 1.2 \times 0.0821 \times 300$ ($\because$ P = 760 torr = 1 atm)
V = 29.556 L

$$d_{N_2O_4} = \frac{m}{V} = \frac{0.8\times 92}{29.556} = 2.490$$

$$d_{NO_2} = \frac{m}{V} = \frac{0.4\times 46}{29.556} = 0.6225$$

d_{mix} = 2.490 + 0.6225 = 3.1125 g/L

13. $3C_{(graphite)} + 4H_{2(g)} \rightarrow C_3H_{8(g)}$
$\Delta_r H° = \Delta_f H°\,(C_3H_8) - \{3\Delta_f H°\,(C) + 4\Delta_f H°(H_2)\}$
$= -103.8 - 0 - 0 = -103.8$ kJ mol^{-1}
$\Delta_r S° = S°_m\,(C_3H_8) - \{3S°_m\,(C) + 4S°_m\,(H_2)\}$
$= 270.2 - \{3 \times 5.70 + 4 \times 130.7\}$
$= 270.2 - 539.9 = -269.7$ J K^{-1} mol^{-1}
$\Delta_r G° = \Delta_r H° - T\Delta_r S°$
$= -103.8 - 298 \times (-269.7 \times 10^{-3}) = -23.43$ kJ mol^{-1}

14. The two conditions under which heat becomes independent of path are
(i) when volume remains constant
(ii) when pressure remains constant.
(i) At constant volume : By first law of thermodynamics,
$\Delta U = q + w$ or $q = \Delta U - w$
$w = -P\Delta V$ $\therefore$ $q = \Delta U + P\Delta V$
But as volume remains constant, $\Delta V = 0$
$\therefore$ $q_v = \Delta U$
As ΔU is a state function. Hence, q_v is a state function.
(ii) At constant pressure : $q_p = \Delta U + P\Delta V$
But $\Delta U + P\Delta V = \Delta H$
$\therefore$ $q_p = \Delta H$
As ΔH is a state function, therefore, q_p is a state function.

15.

	$NH_{3(g)}$	+ $HCl_{(g)}$ $\longrightarrow$	$NH_4Cl_{(s)}$
At, $t=0$	$\frac{1\times 2}{0.08\times 200}$ $=0.125$	$\frac{8\times 0.8}{0.08\times 200}$ $=0.4$	0
After reaction	0	0.275	0.125

Thus, heat produced during reaction,

$Q = n_{NH_4Cl} \times \Delta H = 0.125 \times 43 \times 10^3 = 5375$ J

$\because$ During the formation of 1 mole $NH_4Cl_{(s)}$, heat produced is ΔH. Because this heat is used to increase the temperature of HCl in both the flasks.

Thus, $Q = n \times C_v \times \Delta T$

$5375 = 0.275 \times 20 \times \Delta T \Rightarrow \Delta T = 977.27$ K

$\therefore$ $T_f = 200 + 977.27 = 1177.27$ K

and $P_f = \dfrac{nRT_f}{V} = \dfrac{0.275\times 0.0821\times 1177.27}{1.8}$

= 14.76 atm (Here, $V = 1 + 0.8 = 1.8$ L)

16. (a) (i) $\Delta H = ms\,\Delta T$

= (0.092 cal/g/K) (100 g) [(373 – 283) K] = 828 cal

(ii) Since the specific heat capacity of copper is less than that of aluminium, less heat is required to raise the temperature of a mass of copper by 1 K than is required for an equal mass of aluminium. Hence, the copper gets hotter.

(b) Total heat absorbed

$= \Delta H_{\text{fusion}} + \Delta H_{\text{temp. rise}} + \Delta H_{\text{vap.}}$

$= 10 \times 80 + 10 \times 1 \times 100 + 10 \times 540 = 7200$ cal

17. Suppose the number of moles of gas present at 27°C in flask of volume V at pressure P is n_1, then assuming ideal gas behaviour,

$PV = n_1 R \times 300$ ...(i)

Suppose, n_2 = number of moles at 477°C, then

$PV = n_2 R \times 750$ ...(ii)

From eq. (i) and eq. (ii), we get

$$n_2 = \frac{300}{750}\times n_1 = 0.4\ n_1$$

$\therefore$ 0.6 moles have been expelled out.

OR

The reaction between aluminium and caustic soda is

$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$

$2 \times 27 = 54$ g $\qquad$ 3×22.4 L at STP

$\therefore$ 54 g of Al produces H_2 at S.T.P. = 3 × 22.4 L

0.15 g of Al will produce H_2 at S.T.P.

$$= \frac{3\times 22.4}{54}\times 0.15 = 0.186 \text{ L}$$

Applying ideal gas equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{1\times 0.186}{273} = \frac{0.987\times V_2}{293}$$

$$V_2 = \frac{293}{0.987}\times\frac{1\times 0.186}{273} = 0.2030 \text{ L} = 203 \text{ mL}$$

18. (a) It is clear from the figure that the process has been carried out in infinite steps and therefore, it is an isothermal reversible expansion process.

$$w = -2.303\ nRT \log\frac{V_2}{V_1} = -2.303\ nRT \log\frac{P_1}{P_2}$$

$= -2.303 \times 1 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{ mol}^{-1} \times 298 \text{ K} \times \log 2$

$= -1717.6$ J

(b) At constant temperature,

$P_1V_1 = P_2V_2$

$$P_2 = \frac{P_1V_1}{V_2} = \frac{1\times V_1}{4V_1} = 0.25 \text{ atm}$$

19. (i) Heat of combustion at constant volume,

ΔU = Heat capacity of calorimeter system ×

$$\text{rise in temperature} \times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{16}{0.16} = 8$$

$\Delta U = -885$ kJ mol^{-1}

(ii) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

$\Delta n_g = 1 - 3 = -2$, $T = 300$ K,

$R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}

Heat of combustion at constant pressure,

$\Delta H = \Delta U + \Delta n_g RT$

$= -885 + (-2) \times 8.314 \times 10^{-3} \times 300$

$= -889.988$ kJ mol^{-1}

20. (a) At higher altitudes, the atmospheric pressure decreases. Thus, the pressure outside the balloon decreases. To regain equilibrium with the external pressure, the gas inside, expands to decrease its pressure. Hence, the size of the balloon increases.

(b) In summer, due to higher temperature, the average kinetic energy of the air molecules inside the tyres increases *i.e.*, molecules start moving faster. Hence, the pressure on the walls of the tube increases. If pressure inside is not kept low at the time of inflation, at higher temperature, the pressure may become so high that the tyre may burst.

21. From adiabatic gas equation, $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{\gamma-1}$

Given that, $\gamma = 1.5$, $P_2/P_1 = 27$, $T_1 = 300$ K

Substituting the values,

$$\left(\frac{300}{T_2}\right)^{1.5} = \left(\frac{1}{27}\right)^{1.5-1}$$

After taking log on both sides,

$1.5(\log 300 - \log T_2) = 0.5(\log 1 - \log 27)$

$\log 300 - \log T_2 = -\frac{0.5 \log 27}{1.5}$

$\log T_2 = \log 300 + 0.33 \log 27$

$= 2.477 + 0.4723 = 2.9493$

$\therefore\ T_2 = \text{antilog } 2.9493 = 889.81$

$= (889.81 - 273)°\text{C} = 616.81°\text{C}$

Hence, the rise in temperature

$= 616.81 - 27 = 589.81°\text{C}$

22. (a) Efficiency $= \frac{T_2 - T_1}{T_2}$

$T_2 = 100 + 273 = 373$ K

$T_1 = 25 + 273 = 298$ K

Efficiency $= \frac{373 - 298}{373} = \frac{75}{373} = 0.20 = 20\ \%$

(b) Heat evolved will be different. This is because they have different crystal structures.

23. (a) At higher altitude, atmospheric pressure is low, so generally people have difficulty in breathing therefore, people must need to undergo for medical check-up before going on Amarnath Yatra.

(b) At higher altitude, atmospheric pressure is low. Therefore, the liquid boils at lower temperature.

(c) Knowledge, health concern.

(d) When density of liquid and vapours become the same, the clear boundary between liquid and vapours disappears. This temperature is called critical temperature.

24. (a) The volume of a sphere $= \frac{4}{3}\pi r^3$

where, r is the radius of the sphere.

For N_2 molecule,

$r = 0.2$ nm $= 0.2 \times 10^{-9}$ m $= 2 \times 10^{-8}$ cm

Volume of a molecule of $N_2 = \frac{4}{3} \times \frac{22}{7} \times (2 \times 10^{-8})^3\ \text{cm}^3$

$= 3.35 \times 10^{-23}\ \text{cm}^3$

(b) To calculate the empty space, let us first find the total volume of 1 mole (6.02×10^{23} molecules) of N_2.

Volume of 6.02×10^{23} molecules of N_2

$= 3.35 \times 10^{-23} \times 6.02 \times 10^{23} = 20.17\ \text{cm}^3$

Now, volume occupied by 1 mole of gas at S.T.P.

$= 22.4$ litre $= 22400\ \text{cm}^3$

Empty volume = Total volume of gas – Volume occupied by molecules

$= (22400 - 20.17)\ \text{cm}^3$

$= 22379.83\ \text{cm}^3$

$\therefore$ Percentage empty space $= \frac{\text{Empty space}}{\text{Total volume}} \times 100$

$= \frac{22379.83}{22400} \times 100 = 99.9\ \%$

Thus, 99.9% of space of 1 mole of N_2 at S.T.P is empty.

OR

(a) In an ideal gas, there are no intermolecular forces of attraction and therefore, no force opposes the expansion in vacuum. Hence, no energy is required to overcome these forces. Moreover, when a gas expands against vacuum, work done is zero because $p_{ext} = 0$. Therefore, internal energy of the system does not change, *i.e.*, there is no absorption or evolution of heat.

(b) Total heat change,

$\Delta H = 90.0 \times 540 = 48600$ cal

Now, $\Delta H = \Delta U + P\Delta V$

Here, $\Delta V = (V_{vapour} - V_{liquid}) = V_{vapour}$

(Vol. of liquid is negligible as compared to volume of vapour)

$\Delta H = \Delta U + PV_{vapour} = \Delta U + nRT$

$n = \frac{90}{18} = 5$ mol, $R = 2$ cal K^{-1} mol^{-1}, $T = 373$ K

$\therefore\ \Delta H = \Delta U + 5 \times 2 \times 373$

$\Delta H = \Delta U + 3730$; $\Delta U = \Delta H - 3730$

$= 48600 - 3730 = 44870$ cal

25. (a) (i) $\frac{r_{vapour}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{vapour}}}$; $1.33 = \sqrt{\frac{32}{M_{vapour}}}$

$M_{vapour} = 18.1$

(ii) Molar volume $= \frac{\text{Molar mass}}{\text{Density}}$

$= \frac{18.1}{0.36 \times 10^3} = 50.27 \times 10^{-3}\ \text{m}^3/\text{mol}$

(iii) Compressibility factor,

$$Z = \frac{PV}{RT} = \frac{101325 \times 50.27 \times 10^{-3}}{8.314 \times 500} = 1.225$$

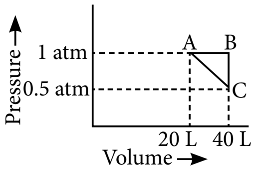
(iv) $Z > 1$, shows that repulsive forces are dominant.

(b) Translational *K.E.* per molecule $= \frac{3}{2} \times \frac{R}{N_A} \times T$

$$= \frac{3}{2} \times \frac{8.314}{6.023 \times 10^{23}} \times 1000 = 2.07 \times 10^{-20} \text{ J}$$

OR

(i) $AB \longrightarrow$ Isobaric process
$BC \longrightarrow$ Isochoric process
$CA \longrightarrow$ Isothermal compression



(ii) Total work $= w_{AB} + w_{BC} + w_{CA}$

$w = -P \times (V_2 - V_1) + 0 + 2.303\, nRT \log(V_2/V_1)$

$= -1 \times (40 - 20) + 0 + 2.303\, P_1V_1 \times \log(V_2/V_1)$ $[nRT = P_1V_1]$

$= -20 + 2.303 \times (20) \log \frac{40}{20}$

$= -20 + (2.303)(20)(0.301029)$

$= -20 + 13.86539574 = -6.13$ L atm

$= \frac{6.13 \times 8.314 \text{ J}}{0.0821} = -620.76$ J

$w = q = -620.76$ J

(iii) In cyclic process :
$\Delta U = 0, \Delta H = 0$ and $\Delta S = 0$

26. (a) Process $A \rightarrow B$ (expansion), $P = 12 \times 10^5$ N m^{-2}, $\Delta V = 8 - 2 = 6$ L $= 6 \times 10^{-3}$m^3

$\therefore$ Work done $= -P\Delta V = -(12 \times 10^5) \times (6 \times 10^{-3})$J $= -7200$ J

Process $B \rightarrow C$, No change in volume, *i.e.*, $\Delta V = 0$

$\therefore$ Work done = 0

Process $C \rightarrow D$ (contraction), $\Delta V = 8 - 2 = 6$ L $= 6 \times 10^{-3}$m^3, $P = 4 \times 10^5$N m^{-2}

$\therefore$ Work done $= P\Delta V = (4 \times 10^5)(6 \times 10^{-3}) = 2400$ J

Process $D \rightarrow A$, No change in volume, *i.e.*, $\Delta V = 0$

$\therefore$ Work done = 0

$\therefore$ Net work done in the complete cyclic process $= -7200 + 2400$ J $= -4800$ J

–ve sign shows that net work has been done by the gas.

(b) The energy of the universe is constant, whereas the entropy of the universe is continuously increasing and tends to maximum.

OR

(a) According to Graham's law of diffusion

$$\frac{r_{mix}}{r_{Kr}} = \sqrt{\frac{M_{Kr}}{M_{mix}}} \Rightarrow 1.16 = \sqrt{\frac{84}{M_{mix}}}$$

$\because\ M_{mix} = 62.425$

	Cl_2	$\rightleftharpoons$	$2Cl$
Initial mole	1		0
Final mole	$1-x$		$2x$

Total moles $= 1 - x + 2x = 1 + x$

$$\therefore\ M_{mix} = \frac{2x(35.5) + (1-x) \times 71}{1+x} = 62.425$$

$$\frac{71}{1+x} = 62.425$$

$x = 0.1373 = 13.7\%$ dissociated

(b) For 1 mol of a gas, the van der Waals' equation is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Ignoring b, we get (given volume of gas molecule is negligible)

$$\left(p + \frac{a}{V_m^2}\right)V_m = RT \Rightarrow pV_m + \frac{a}{V_m} = RT$$

$$\frac{pV_m}{RT} + \frac{a}{V_mRT} = 1 \Rightarrow Z = \frac{pV_m}{RT} = 1 - \frac{a}{V_mRT} \quad \text{...(i)}$$

$$Z = \frac{pV_m}{RT} = 0.5 \Rightarrow V_m = \frac{0.5RT}{p}$$

Now, from eq. (i), $0.5 = 1 - \frac{a}{(0.5RT/p)RT}$

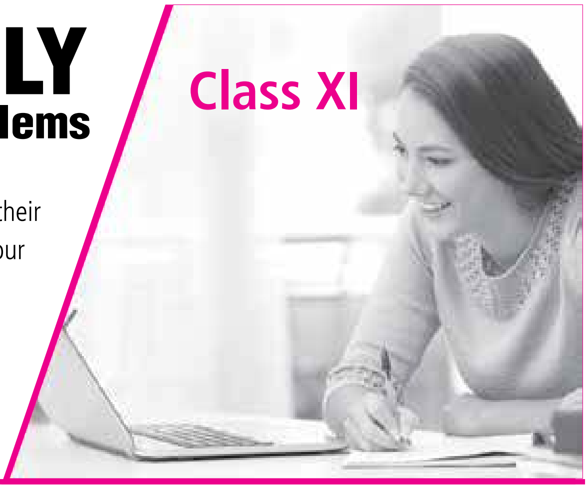
$$a = (0.5)\left(\frac{0.5RT}{p}\right)RT = 0.25\frac{R^2T^2}{p}$$

Substituting the given values, we get

$$a = (0.25)\left[\frac{(0.082 \text{ L atm K}^{-1}\text{mol}^{-1})^2(273 \text{ K})^2}{100 \text{ atm}}\right]$$

$= 1.2528$ L^2 atm mol^{-2}

MPP-5 MONTHLY Practice Problems



This specially designed column enables students to self analyse their extent of understanding of specified chapter. Give yourself four marks for correct answer and deduct one mark for wrong answer.

Self check table given at the end will help you to check your readiness.

Equilibrium

Total Marks : 120 **Time Taken : 60 Min.**

NEET / AIIMS

Only One Option Correct Type

1. Vapour density of PCl_5 at 200 °C is 70. Determine the degree of dissociation of PCl_5 at this temperature.
(a) 48.9% (b) 57.9% (c) 38.8% (d) 46.1%

2. Starting with 1 mol of $O_{2(g)}$ and 2 mol of $SO_{2(g)}$ the equilibrium for the formation of $SO_{3(g)}$ was established at a certain temperature. If V is the volume of the vessel and $2x$ is the number of moles of $SO_{3\,(g)}$ present, the equilibrium constant will be
(a) $\frac{x^2V}{(1-x)^3}$ (b) $\frac{4x^2V}{(2-x)(1-x)}$
(c) $\frac{(1-x)^3}{2V}$ (d) $\frac{x^2V}{(2-x)(1-x)V}$

3. Which one of the following solutions will have pH close to unity?
(a) 100 mL of M/10 HCl + 100 mL of M/10 NaOH
(b) 55 mL of M/10 HCl + 45 mL of M/10 NaOH
(c) 10 mL of M/10 HCl + 90 mL of M/10 NaOH
(d) 75 mL of M/5 HCl + 25 mL of M/5 NaOH

4. When different types of salts have nearly same solubility product constant (K_{sp}) which is lesser than K_{sp} value of one salt, then the most soluble salt is the one
(a) which produces maximum number of ions
(b) which produces minimum number of ions
(c) which produces more charge on ion
(d) none of these.

5. Consider the following reactions in which all the reactants and the products are in gaseous state :
$2PQ \rightleftharpoons P_2 + Q_2\,;\ K_1 = 2.5 \times 10^5$
$PQ + 1/2R_2 \rightleftharpoons PQR\,;\ K_2 = 5 \times 10^{-3}$
The value of K_3 for the equilibrium :
$1/2P_2 + 1/2Q_2 + 1/2R_2 \rightleftharpoons PQR$, is
(a) 2.5×10^{-3} (b) 2.5×10^3
(c) 1.0×10^{-5} (d) 5.0×10^3

6. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid,
$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$
The set that characterises the conjugate acid-base pairs is
(a) (HCl, CH_3COOH) and ($CH_3COOH_2^+$,Cl^-)
(b) (HCl, $CH_3COOH_2^+$) and (CH_3COOH, Cl^-)
(c) ($CH_3COOH_2^+$, HCl) and (Cl^-,CH_3COOH)
(d) (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH)

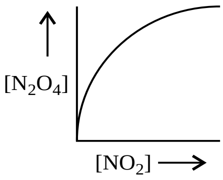
7. One mole of $N_2O_{4(g)}$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $N_2O_{4(g)}$ decomposes to $NO_{2(g)}$. The resultant pressure is
(a) 1.2 atm (b) 2.4 atm (c) 2.0 atm (d) 1.0 atm

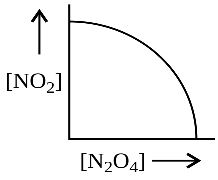
8. A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionisation constant of pyridine.
(a) 1.8×10^{-9} (b) 2.1×10^{-8}
(c) 1.5×10^{-9} (d) 1.0×10^{-9}

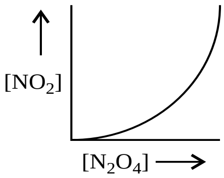
9. For a reaction $2A + B \rightleftharpoons C + D$, the value of K_p will be :
(a) $K_p = \frac{n_C n_D}{n_A^2 n_B} \frac{V_P}{RT^2}$ (b) $K_p = \frac{n_C n_D}{n_A^2 n_B} \frac{P}{RT}$
(c) $K_p = \frac{n_C n_D}{n_A^2 n_B} \frac{RT^2}{V_P}$ (d) $K_p = \frac{n_C n_D}{n_A^2 n_B} \frac{V_P}{RT}$

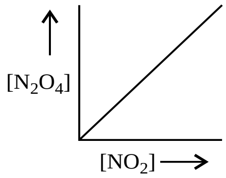
10. The equilibrium constant for the following reaction,
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \text{ is } K = \frac{[NO_2]^2}{[N_2O_4]}$$

Which of the following graphs is correct?

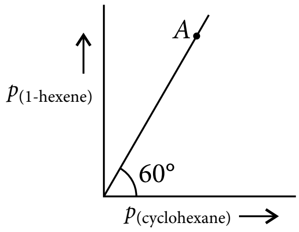
(a) 

(b) 

(c) 

(d) 

11. For the following isomerisation reaction :
Cyclohexane $\rightleftharpoons$ 1-Hexene, $K = 1.732$
Which of the following statements holds good at point 'A'?



(a) $Q > K$
(b) $Q < K$
(c) $Q = K = 1$
(d) $Q = K = 1.732$

12. The decreasing base strength of $OH^-, NH_2^-, HC{\equiv}C^-$ and $CH_3CH_2^-$ is
(a) $CH_3CH_2^- > NH_2^- > HC{\equiv}C^- > OH^-$
(b) $HC{\equiv}C^- > CH_3CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > HC{\equiv}C^- > CH_3CH_2^-$
(d) $NH_2^- > HC{\equiv}C^- > OH^- > CH_3CH_2^-$

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. **Assertion :** K_p can be equal to or less than or even greater than the value of K_c.
Reason : $K_p = K_c\,(RT)^{\Delta n}$

14. **Assertion :** On cooling a freezing mixture, colour of the mixture turns to pink from deep blue for a reaction,
$$[Co(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons [CoCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$$
Reason : Reaction is endothermic so on cooling, the reaction moves to backward direction.

15. **Assertion :** Common salt is added during manufacturing of soap.
Reason : Common salt helps in the formation of soap.

JEE MAIN / JEE ADVANCED

Only One Option Correct Type

16. The equilibrium constants K_{p_1} and K_{p_2} for the reactions : $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is
(a) 1 : 9 (b) 1 : 36 (c) 1 : 1 (d) 1 : 3

17. Which of the following is not correct about the percentage ionisation of BOH?
(a) $\dfrac{K_w[H^+]}{K_b + K_w}$ (b) $100 \times \sqrt{\dfrac{K_b}{C}}$
(c) $\dfrac{100}{1 + 10^{(pK_b - pOH)}}$ (d) $\dfrac{K_b \times 100}{K_b + OH^-}$

18. The pH of pure water at 25 °C and 35 °C are 7 and 6 respectively. The heat of formation of water from H^+ and OH^- is
(a) 84.551 kcal mol^{-1} (b) –84.551 kcal mol^{-1}
(c) 74.551 kcal mol^{-1} (d) –74.551 kcal mol^{-1}

19. Ammonia under a pressure of 15 atm at 27 °C is heated to 347 °C in a closed vessel in the presence of a catalyst. Under the conditions, NH_3 is partially decomposed according to the equation, $2NH_3 \rightleftharpoons N_2 + 3H_2$. The vessel is such that the volume remains effectively constant whereas pressure increases to 50 atm. Calculate the percentage of NH_3 actually decomposed.
(a) 65% (b) 61.3% (c) 62.5% (d) 64%

More than One Options Correct Type

20. When two reactants, A and B are mixed to give two products, C and D, the reaction quotient, (Q) at the initial stages of the reaction
(a) is zero (b) decreases with time
(c) is independent of time
(d) increases with time.

21. Which of the following are heterogeneous systems?
(a) Ice $\rightleftharpoons$ Water (b) Water $\rightleftharpoons$ Liquid
(c) $S_{Rhombic} \rightleftharpoons S_{Monoclinic}$
(d) $C_{Diamond} \rightleftharpoons C_{Amorphous}$

22. A reaction $S_{8(g)} \rightleftharpoons 4S_{2(g)}$ is carried out by taking 2 moles of $S_{8(g)}$ and 0.2 mole of $S_{2(g)}$ in a reaction vessel of 1 litre at 627 °C. Which of the following are correct if $K_c = 6.30 \times 10^{-6}$?
(a) Reaction quotient is 8×10^{-4}
(b) Reaction proceeds in backward direction
(c) $K_p = 2.55$ atm^3
(d) Reaction proceeds in forward direction

23. The solubility of a sparingly soluble salt A_xB_y in water at 25 °C = 1.4×10^{-4} M. The solubility product is 1.1×10^{-11}. The possibilities are

(a) $x = 1, y = 2$ (b) $x = 2, y = 1$
(c) $x = 1, y = 3$ (d) $x = 3, y = 1$

Integer Answer Type

24. In the study of reaction,

$$A + 2B \rightleftharpoons 2C + D$$

A and B were mixed in a reaction vessel at 300 K. The initial concentration of B was 1.5 times the initial concentration of A. After the equilibrium has been attained, the equilibrium concentrations of A and D were equal. The value of equilibrium constant at 300 K is

25. In 1 L saturated solution of AgCl [$K_{sp(\text{AgCl})} = 1.6 \times 10^{-10}$], 0.1 mol of CuCl [$K_{sp(\text{CuCl})} = 1 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. The value of x is

26. A mixture of N_2 and H_2 in the molar ratio 1 : 3 attains equilibrium when 50% of mixture has reacted. If P is the total pressure of the mixture, the partial pressure of NH_3 formed is P/y. The value of y is

Comprehension Type

The concentration of hydrogen ion is a measure of acidity or alkalinity of a solution.

For monobasic acids :

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+;\ \alpha = \sqrt{\frac{K_a}{C}}$$

where, K_a = Dissociation constant of acid
C = Molarity of acid

$[H^+] = C\alpha$, $[H^+] = \sqrt{K_aC}$

pH of a weak acid can be calculated using $[H^+]$ by any of above methods.

$[H^+]_{\text{Total}} = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$ (when two weak acids are mixed)

$[H^+]$ of polyprotic acid (Weak, H_3A) (has dissociation constants $K_{a_1} >> K_{a_2} >> K_{a_3}$) ; will be contributed by first dissociation at the most.

27. What will be the sulphide ion concentration of a dilute solution that has been saturated with 0.1 M H_2S if the pH of the solution is 3?
(Given : $K_{a_1} = 1 \times 10^{-7}$; $K_{a_2} = 1.3 \times 10^{-13}$)

(a) 1.25×10^{-11} (b) 1.3×10^{-13}
(c) 1.45×10^{-9} (d) 1.3×10^{-15}

28. The pH of 0.01 M HCOOH ($K_a = 1.4 \times 10^{-4}$) will be

(a) 2.928 (b) 3.296 (c) 4.962 (d) 5.926

Matrix Match Type

29. Match the Column I with Column II and choose the correct option using the codes given below.

Column I (Salt)	Column II (Solubility product)
(A) Zirconium phosphate	(p) $27\ S^4$
(B) Aluminium phosphate	(q) $108\ S^5$
(C) Calcium phosphate	(r) $6912\ S^7$
(D) Sodium phosphate	(s) S^2

	A	B	C	D
(a)	s	r	q	p
(b)	r	s	q	p
(c)	p	r	s	q
(d)	q	r	s	p

30. Match the Column I with Column II and choose the correct option using the codes given below.

Column I (Salt)	Column II (Degree of hydrolysis)
(A) NaCl	(p) $h = \sqrt{\frac{K_w}{C \cdot K_b}}$
(B) CH_3COONa	(q) $h = \sqrt{\frac{K_w}{K_a \times K_b}}$
(C) NH_4Cl	(r) No hydrolysis
(D) CH_3COONH_4	(s) $h = \sqrt{\frac{K_w}{C \cdot K_a}}$

	A	B	C	D
(a)	p	q	s	r
(b)	r	s	p	q
(c)	q	r	s	p
(d)	p	r	s	q

Keys are published in this issue. Search now! ☺

SELF CHECK

No. of questions attempted ……
No. of questions correct ……
Marks scored in percentage ……

Check your score! If your score is

> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

NEET | JEE ESSENTIALS

Class XII

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Unit 3 General Principles and Processes of Isolation of Elements | *p*-Block Elements (Group 15 to 18)

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

General Introduction

The percentage of different elements in the earth crust are : O - 49%, Si - 26%, Al - 7.5%, Fe - 4.2%, Ca - 3.2%, Na - 2.4%, K - 2.3%, Mg - 2.5%, H - 1%

Metals

- Native State: Like Au, Ag, Pt, S, O, N, noble gases, etc.
- Combined State: Highly reactive metals occur as oxides, carbonates, sulphides and halides, etc.

Ores / Minerals

Combined state	Element	Ore/mineral
Oxides	Fe	Haematite (Fe_2O_3) Magnetite (Fe_3O_4) Limonite ($Fe_2O_3 \cdot 3H_2O$) Chromite ($FeO \cdot Cr_2O_3$)
	Al	Bauxite ($Al_2O_3 \cdot 2H_2O$) Diaspore ($Al_2O_3 \cdot H_2O$) Corundum (Al_2O_3)
	Zn	Zincite (ZnO)
	Cu	Cuprite (Cu_2O)
Carbonates	Ca	Calcite ($CaCO_3$)
	Mg	Magnesite ($MgCO_3$)
	Cu	Malachite [$CuCO_3 \cdot Cu(OH)_2$]
	Zn	Calamine ($ZnCO_3$)
	Fe	Siderite ($FeCO_3$)
Sulphides	Fe	Iron pyrite (FeS_2)
	Cu	Copper glance (Cu_2S)
	Hg	Cinnabar (HgS)
	Zn	Zinc blende (ZnS)
	Pb	Galena (PbS)
	Ag	Argentite or Silver glance (Ag_2S)
Halides	Na	Common salt or Rock salt (NaCl)
	Al	Cryolite (Na_3AlF_6)
	K, Mg	Carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$)
	Ag	Horn silver (AgCl)

EXTRACTION OF METALS

Ore

Powdered ore

Removal of gangue

- Hydraulic washing (for carbonate and oxide ores)
- Froth floatation (for sulphide ores)
- Electromagnetic separation (for magnetic ores)
- Electrostatic separation (for PbS and ZnS)
- Leaching (for Ag, Al, Au)

Concentrated ore

- Calcination (for carbonate and hydroxide ores)
- Roasting (for sulphide ores)

Metal oxide

- Smelting
- Reduction with Mg, Al
- Reduction with H_2, water gas

Crude metals

Refining

- Liquation
- Poling
- Electrorefining
- Zone refining
- Vapour phase refining
- Chromatography

Pure metal

CONCENTRATION OF ORE

Froth floatation

- Based on preferential wetting of ore particles by oil (pine oil).
- Ore particles become light and form froth.
- Froth can be stabilised by stabilisers (aniline or cresols).

Electromagnetic separation

- Conveyor belt moving over two rollers, one of which is magnetic in nature.
- Magnetic ores are attracted by the magnetic roller.

Leaching

- It involves the treatment of the powdered ore with a suitable reagent so as to make it soluble while impurities remain insoluble.

Leaching of bauxite (Baeyer's process) :

$$Al_2O_3.2H_2O + 2NaOH + H_2O \xrightarrow{473\text{-}523\ K} \underset{\text{Sodium aluminate}}{2Na[Al(OH)_4]}$$

$$2Na[Al(OH)_4] + 2CO_2 \rightarrow Al_2O_3.xH_2O\downarrow + 2NaHCO_3$$

$$Al_2O_3.xH_2O \xrightarrow{1473\ K} Al_2O_3 + xH_2O$$

Leaching of silver or gold (Mac-Arthur Forest cyanide process) :

$$4Ag + 8NaCN + O_2 + 2H_2O \rightarrow 4Na[Ag(CN)_2] + 4NaOH$$

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$$

Conversion of ore into metal oxide

Calcination

- Heating of ore below its fusion temperature in absence of air.
- For carbonate and hydroxide ores.
- In reverberatory furnace. *e.g.*, $\underset{\text{Calamine}}{ZnCO_3} \xrightarrow{\Delta} \underset{\text{Zinc oxide}}{ZnO} + CO_2\uparrow$

Roasting

- Ore is heated in presence of air.
- For sulphide ores.
- In reverberatory or blast furnace. *e.g.*, $2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2\uparrow$

Reduction of metallic oxide to free metal

Pyrometallurgy
Heating of metal oxide with a suitable reducing agent.

Smelting
Reduction of oxides with carbon.
$M_xO_y + yC \longrightarrow xM + yCO$

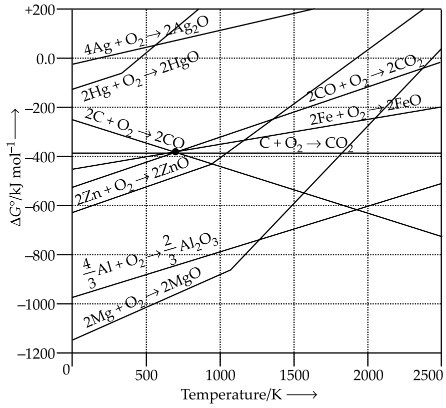
By aluminium (Goldschmidt alumino thermite process)
Reduction of metal oxide to metal by aluminium powder. $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$

Self reduction (Auto-reduction)
Sulphide ores of less electropositive metals like Hg, Pb, Cu, etc. are heated in air.

Electrolytic reduction
The oxides, hydroxides or chlorides of highly electropositive metals like Na, K, Mg, Ca and Al are extracted by electrolytic method, in their fused state. Electrolysis of this method is based on equation $\Delta G° = -nFE°$.

THERMODYNAMIC PRINCIPLES IN EXTRACTION OF METALS

- The free energy change (ΔG), occurring during the reduction processes help in deciding the suitable method for reduction, is given by $\Delta G = \Delta H - T\Delta S$; where, ΔH = enthalpy change; ΔG = Gibbs free energy change; T = temperature; ΔS = entropy change.
- Greater the negative value of ΔG, higher is the reducing power of an element.
- For the reduction of a metal oxide with a reducing agent, the plot of $\Delta G°$ *vs* temperature is studied, which is called Ellingham diagram.



CHARACTERISTICS OF ELLINGHAM DIAGRAM

- $\Delta G°$ becomes more positive when temperature increases, *i.e.*, stability of oxides decreases.
- A metal will reduce the oxide of other metals which lie above it in Ellingham diagram, *i.e.*, the metals for which the free energy of formation ($\Delta G°$) of their oxides is more negative can reduce those metal oxides which has less negative $\Delta G°$. Thus, Al reduces FeO, CrO and NiO in thermite reduction but it will not reduce MgO at temperature below 1773 K.
- CO is more effective reducing agent below 1073 K and above 1073 K coke is more effective reducing agent, *e.g.*, CO reduces Fe_2O_3 below 1073 K but above it, coke reduces Fe_2O_3.

Refining (Purification of Crude Metal)

Distillation Process
- Used for volatile metals like Zn, Cd, Hg, etc.

Liquation process
- Based on difference in fusibility of metal and impurities. Used for Bi, Sn, Pb, Hg, etc.

Electrolytic refining
Impure metal - Anode
Pure metal - Cathode
On passing current, pure metal is deposited on cathode. Used for Cu, Ag, Au, Ni, etc.

Chromatographic process
- Based on adsorption of components of a mixture.

Vapour phase refining

Mond's process
Impure Nickel + CO $\xrightarrow{60-80°C}$ $Ni(CO)_4$ $\xrightarrow{180°C}$ Ni + 4CO
(Pure)

van Arkel method
For Ti, Zr, Hf, etc.
Impure metal + I_2 $\longrightarrow$ Metal iodide (vapours) $\xrightarrow{\text{heating}}$ Metal + I_2
(Pure)

Zone refining
Impurities are more soluble in molten state than in solid state of metal. Used for semiconductors like Si, Ge, Ga, etc.

Cupellation

Bassemerisation

Poling

Extraction of Al and Zn

Al Extraction

Step 1 : Purification of bauxite ore

Baeyer's Process | Hall's Process | Serpeck's Process

Step 2 : Electrolytic reduction of pure alumina
Step 3 : Refining of Al by Hoope's process

Zn Extraction

Step 1 : Concentrated by froth floatation process
Step 2 : Roasting
Step 3 : Reduction : By carbon

$$ZnO + C \rightarrow Zn + CO$$

Step 4 : Purification by distillation

INFO SHOTS

Perovskite solar cells !

A perovskite is an unique crystal structure, consisting of formamidinium with multiple cations and mixed halide anions. A perovskite solar cell (PSC) is a type of solar cell, which includes the perovskite structured compound, most commonly a hybrid organic-inorganic lead or tin halide based material, as the light harvesting active layer. These solar cells not only show relatively high photovoltaic energy conversion efficiencies (above 22%), but can be also easily fabricated using cheap inorganic-organic perovskite compounds.

p-BLOCK ELEMENTS (GROUP 15 TO 18)

PHYSICAL PROPERTIES

Group-15

Electronic configuration : ns^2np^3; (n = 2 to 6)

Metallic nature : Increases with increase in atomic number.

Ionic/Atomic radii : Increase down the group.

Ionisation energy : Decreases down the group. For an element; $I.E._1 < I.E._2 < I.E._3$

Allotropy : All elements except N and Bi, show allotropy.

Oxidation states : +3 and +5; N and P also show (–3) oxidation state.

Electronegativity : Decreases down the group.

Group-16

Electronic configuration : ns^2np^4; (n = 2 to 6)

Metallic nature : Increases with increase in atomic number.

Ionic/Atomic radii : Smaller than group-15 elements and increase down the group.

Ionisation energy : Lower than group-15 elements (due to half filled configuration of group-15 elements) and increases down the group.

Allotropy : All elements exhibit allotropy.

Electronegativity : Higher than group-15 elements and decreases down the group. O is second most electronegative element.

Oxidation states : +2, +4

Oxygen commonly shows –2 oxidation state.

Group-17

Electronic configuration : ns^2np^5; (n = 2 to 6)

Oxidising nature : Standard reduction potential of halogens are positive and decreases from fluorine to iodine.

F_2 is strongest oxidising agent while I_2 is the weakest.

Ionic/Atomic radii : Halogens have lowest atomic radii in their respective period which increase down the group.

Ionisation energy : They have very high ionisation energy and decreases down the group.

Electronegativity : Halogens are highly electronegative.

Oxidation states : F (–1 only)

Cl, Br, I show –1, +1, +3, +5, +7 oxidation states.

Group-18

Electronic configuration : ns^2np^6; (n = 2 to 6), (stable, fully filled, very less reactive).

Atomic radii : Exceptionally high as atomic radii correspond to van der Waals' radii.

Ionisation enthalpy : High value due to stable fully filled configuration.

Adsorption over charcoal : Except helium, these gases can be adsorbed by coconut charcoal at suitable temperatures.

Chemical Properties

Oxides

Group-15

(X_2O_3, X_2O_4, X_2O_5 type)

N_2O_3, P_2O_3, As_2O_3, Sb_2O_3, Bi_2O_3 → Acidic nature decreases

N_2O_4

N_2O_5

↓ Acidic nature increases

Group-16

(MO_2 and MO_3 type)

$\underbrace{SO_2 \quad SeO_2}_{\text{Acidic}} \longrightarrow \underbrace{TeO_2 \quad PoO_2}_{\text{Amphoteric}}$

Water solubility decreases

Acidic character decreases

$SO_2 \downarrow SO_3$ Acidic character increases

Group-17

Called oxygen fluorides as fluorine is more electronegative than oxygen $\left\{ \begin{array}{l} OF_2 \\ O_2F_2 \end{array} \right.$

Oxides

Cl_2O	Br_2O	I_2O_7
ClO_2	BrO_2	
Cl_2O_6	BrO_3	
Cl_2O_7		

↓ Acidic nature increases

Oxyacids

Group-15

Oxyacids of N	$H_2N_2O_2$ (+1) (Hyponitrous acid)	HNO_2 (+3) (Nitrous acid)	HNO_3 (+5) (Nitric acid)
Oxyacids of P	H_3PO_2(+1) (Monobasic) Phosphinic acid	H_3PO_3(+3) (Dibasic) Orthophosphorous acid	$H_4P_2O_6$ (+4) (Tetrabasic) Hypophosphoric acid
	H_3PO_4(+5) (Tribasic) Orthophosphoric acid	HPO_3(+5) (Monobasic) Metaphosphoric acid	$H_4P_2O_7$(+5) (Tetrabasic) Pyrophosphoric acid
Oxyacids of As and Bi	H_3AsO_3(+3) Arsenious acid	H_3AsO_4(+5) Arsenic acid	$HBiO_3$(+5) Metabismuthic acid

Group-16

Oxyacids of S	H_2SO_3(+4) (Dibasic) Sulphurous acid	H_2SO_4(+6) (Dibasic) Sulphuric acid	$H_2S_2O_3$(+6, –2) (Dibasic) Thiosulphuric acid
$H_2S_2O_7$(+6) (Dibasic) Pyrosulphuric acid	$H_2S_2O_6$(+6) (Dibasic) Dithionic acid	$H_2S_2O_8$(+6) (Dibasic) Peroxodisulphuric acid	H_2SO_5(+6) (Dibasic) Peroxomonosulphuric acid

Group-17

Oxyacids of F	HOF (+1) (Hypofluorous acid)	—	—	—
Oxyacids of Cl	HOCl (+1) (Hypochlorous acid)	$HClO_2$ (+3) Chlorous acid	$HClO_3$ (+5) Chloric acid	$HClO_4$ (+7) Perchloric acid
Oxyacids of Br	HOBr (+1) (Hypobromous acid)	—	$HBrO_3$ (+5) Bromic acid	$HBrO_4$ (+7) Perbromic acid
Oxyacids of I	HOI (+1) Hypoiodous acid	—	HIO_3 (+5) Iodic acid	HIO_4 (+7) Periodic acid

Hydrides

NH_3	PH_3	AsH_3	SbH_3	BiH_3
H_2O	H_2S	H_2Se	H_2Te	
HF	HCl	HBr	HI	

$\longrightarrow$

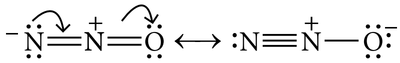
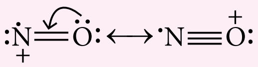
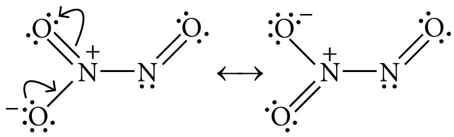
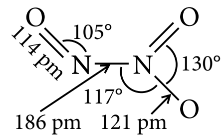
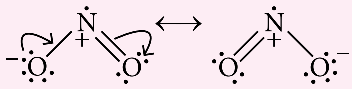
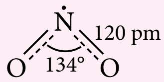
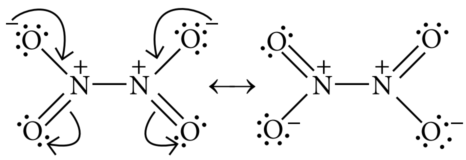
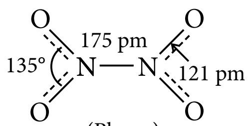
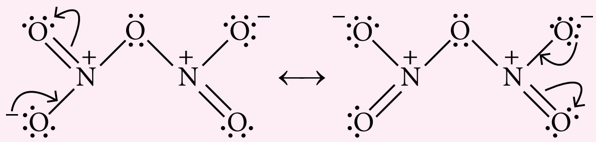
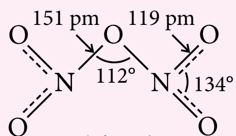
Bond length increases
Thermal stability decreases
Acidic strength increases
Reducing nature increases

Abnormal Behaviour

N, O and F show different properties than their respective period elements due to

- small size
- high electronegativity
- absence of vacant *d*-orbitals.

Oxides of Nitrogen

Formula	Resonance Structures	Bond Parameters
N_2O		$N{\equiv}N{-}O$ 113 pm 119 pm (Linear)
NO		$:N \overset{...}{=} O:$ 115 pm (Linear)
N_2O_3		 (Planar)
NO_2		 (Angular)
N_2O_4		 (Planar)
N_2O_5		 (Planar)

Important Compounds

Dinitrogen (N_2)

- **Preparation :**

$$NH_4Cl + NaNO_2 \xrightarrow{\text{heat}} N_2\uparrow + 2H_2O + NaCl$$
$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{heat}} N_2\uparrow + 4H_2O + Cr_2O_3$$
$$Ba(N_3)_2 \xrightarrow{\text{heat}} Ba + 3N_2\uparrow$$

- **Properties :** Colourless, odourless, tasteless, non-toxic, unreactive due to triple bond; $N{\equiv}N$.
- **Uses :** For manufacturing of HNO_3, NH_3, etc.

Ammonia (NH_3)

- **Preparation :** By Haber's process,

$$N_2 + 3H_2 \underset{773\text{ K}}{\overset{200 \times 10^5\text{ Pa}}{\rightleftharpoons}} 2NH_3;\ \Delta_f H = -46.1\text{ kJ/mol}$$

- **Properties :** Its aqueous solution is basic in nature.

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

- **Uses :** For manufacturing of nitrogenous fertilizers, HNO_3, Na_2CO_3, etc.

CONCEPT MAP CLASS XI

Titrimetric / Volumetric Analysis

Titrimetric analysis has a wide applications in the various fields. It is used to determine the acid content of alcoholic beverages, calcium content in dairy products, total water hardness, vitamin C in fruit juices, etc.

Redox Reactions

Redox reactions are very important in day to day life, these found vast applications in photosynthesis, production of chemicals, extraction of metals, electrochemical cells and quantitative analysis. Some important reduction processes are discussed here.

CONCEPT MAP CLASS XII

Titrimetric / Volumetric Analysis

Simple Titration

- **Acid-base titration :** The concentration of an acid is estimated by adding a solution of standard base. The equivalence point is detected by adding a few drops of suitable indicator to the acid solution.
- **Redox titration :** The concentration of oxidant is estimated by adding reductant or vice versa. For example, Fe^{2+} ions can be estimated by titrating against acidified $KMnO_4$ solution.
- **Precipitation titration :** Cations and anions combine to form a compound of very low solubility.
  $AgNO_3 + NaCl \rightarrow \underset{\text{(White ppt.)}}{AgCl} + NaNO_3$
- **Complexometric titration :** Titrate combines with the titrant to form a complex salt.
  $CuSO_4 + 4NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

If a mixture of NaOH & $NaHCO_3$ is taken

- Equivalents of NaOH = equivalents of HCl required upto phenolphthlein end point.
- Equivalents of $NaHCO_3$ = equivalents of HCl required from phenolphthlein to methyl orange end point.

If a mixture of Na_2CO_3 & $NaHCO_3$ is taken

- 1/2 Equivalents of Na_2CO_3 (n = 2) = equivalents of HCl required upto phenolphthalein end point.
- 1/2 Equivalents of Na_2CO_3 (n = 2) + equivalents of $NaHCO_3$ (n = 1) initially = Equivalents of HCl required from phenolphthalein end point to methyl orange end point.

Back Titration

Reactant A of known concentration is titrated with reactant B (V_1 litre) of known concentration.

Equivalents of B reacted with $A = N_1V_1$

In another flask, reactant C of unknown concentration is reacted with A and excess of A is titrated with B (V_2 litre).

Equivalents of B reacted with excess of $A = N_1V_2$

Equivalents of pure $C = N_1V_1 - N_1V_2$

Moles of pure $C = \dfrac{N_1V_1 - N_1V_2}{n}$

Here, n-factor

For acids, n = basicity of acid

For bases, n = acidity of base

In case of redox reactions :

n-factor = change in oxidation number per molecule = total number of electrons transferred per mole

Mass of pure $C = \dfrac{N_1V_1 - N_1V_2}{n} \times$ Molar mass of C

% Purity of $C = \dfrac{N_1V_1 - N_1V_2}{n} \times \dfrac{\text{Molar mass of } C}{w} \times 100$

where, N_1 = Normality of B, w = Mass of C

In the given calculation, we have taken alkali mixture of NaOH and Na_2CO_3 but other alkali mixtures can also be taken.

If a mixture of NaOH, Na_2CO_3 & $NaHCO_3$ is taken

- Equivalents of NaOH + 1/2 equivalents of Na_2CO_3 (n = 2) = Equivalents of HCl required upto phenolphthalein end point
- 1/2 equivalents of Na_2CO_3 (n = 2) + Equivalents of $NaHCO_3$ initially (n = 1) = Equivalents of HCl required from phenolphthalein end point to methyl orange end point.

Double Titration

The purpose of double titration is to determine the percentage composition of an alkali mixture or an acid mixture.

Process :

- Dissolve mixture of Na_2CO_3 and NaOH in water to make alkaline solution, add two indicators phenolphthalein and methyl orange.
- Now this solution is titrated against HCl.

Reactions Taking Place

$NaOH + HCl \rightarrow NaCl + H_2O$ ...(i)

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ ...(ii)

(Phenolphthalein changes colour)

$NaHCO_3 + HCl \rightarrow H_2CO_3 + NaCl$ ...(iii)

(Methyl orange changes colour)

Calculations

At methyl orange end point :

- Moles of HCl consumed by $NaHCO_3$ $= M_1V_2$ = Moles of $NaHCO_3$ formed from Na_2CO_3 = Moles of Na_2CO_3 in the mixture
- Mass of Na_2CO_3 in the mixture = $M_1V_2 \times 106$
- % of Na_2CO_3 in mixture = $\dfrac{M_1V_2 \times 106}{w} \times 100$

At phenolphthalein end point :

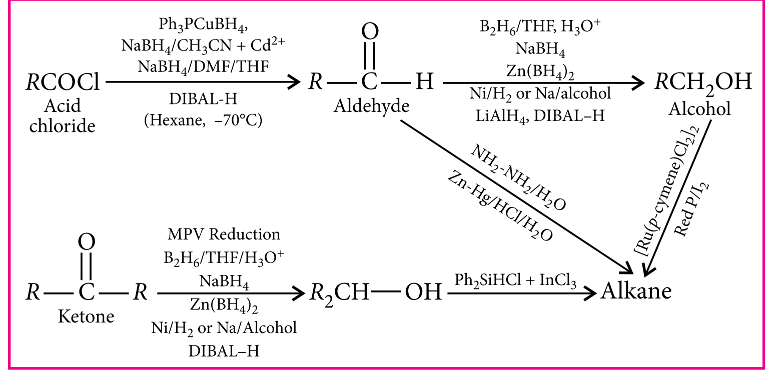
- Moles of HCl used in eq. (i) $= M_1V_1 - M_1V_2$ = Moles of NaOH
- Mass of NaOH $= (M_1V_1 - M_1V_2) \times 40$
- % of NaOH $= \dfrac{(M_1V_1 - M_1V_2) \times 40}{w} \times 100$

where, V_1 = volume of HCl used when phenolphthalein changes colour, V_2 = volume of HCl required from phenolphthalein colour change to methyl orange colour change

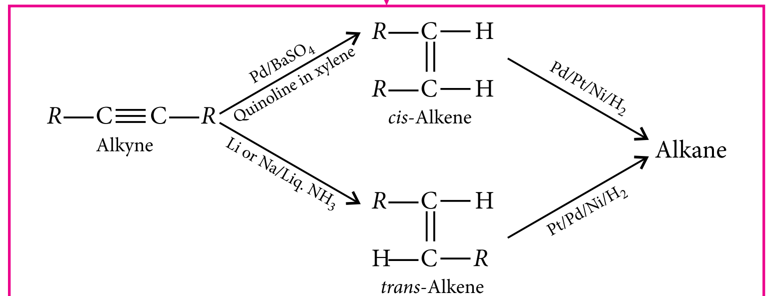
w = Mass of Na_2CO_3-NaOH mixture

Reduction Processes

Reduction of Oxygen Containing Compounds



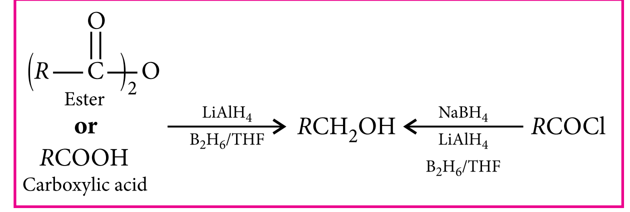
Reduction of Unsaturated Compounds



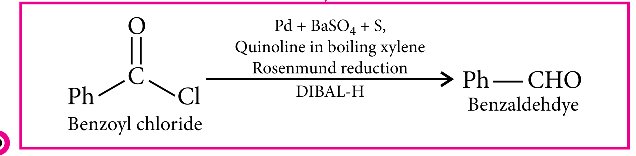
Important Named Reduction Reactions and Reagents

- Zn—Hg/H_2O ⇒ Clemmensen reduction
- NH_2—NH_2/H_2O ⇒ Wolff-Kishner reduction
- Al(O—CH$(CH_3)_2)_3$ + CH_3CH(OH)—CH_3 ⇒ Meerwein-Ponndorf-Verley reduction (MPV Reduction)
- DIBAL—H ⇒ Di-*iso*-butyl aluminium hydride (Highly reactive, hard to control, explodes on heating, grinding or on exposure to water)
- $H_2[SnCl_4]$ ⇒ Stephen's reduction (RCN to $RCHO$)
- Pd + $BaSO_4$ + quinoline in boiling xylene ⇒ Lindlar's catalyst
- Reduction of alkynes to *trans*-alkene using Li, Na/Liq. NH_3 ⇒ Birch reduction

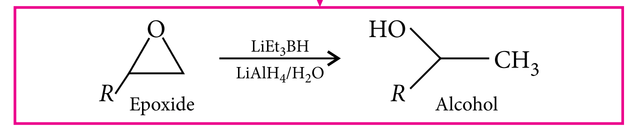
Reduction to Alcohol



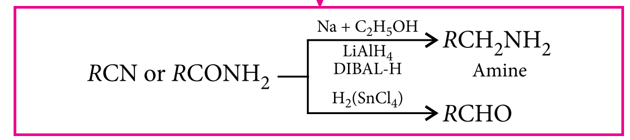
Reduction of Benzoyl Chloride



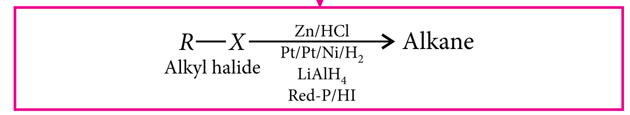
Reduction of Epoxide



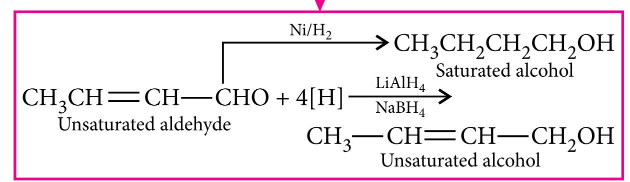
Reduction of N-containing Compounds



Reduction of Halides



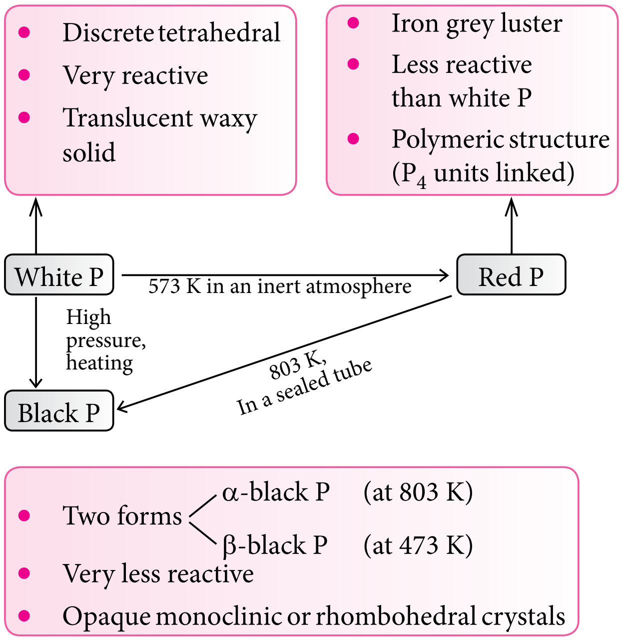
Reduction of Unsaturated Aldehydes

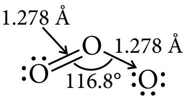


Nitric Acid (HNO_3)

- **Preparation :** By Ostwald process,
  $4NH_3 + 5O_2 \xrightarrow[500\text{ K, 9 bar}]{\text{Pt, Rh gauge}} 4NO + 6H_2O$
  $2NO + O_2 \rightleftharpoons 2NO_2$
  $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$
- **Properties :** It is a strong oxidising agent as it decomposes to give nascent oxygen easily.
- **Oxidation of non-metals :**
  $2HNO_3\text{ (conc.)} \longrightarrow H_2O + 2NO_2 + [O]$
  $2HNO_3\text{ (dil.)} \longrightarrow H_2O + 2NO + 3[O]$
  $S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$
  $C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$
  $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$
  $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$
- The concentrated nitric acid renders metals like iron, cobalt, nickel, chromium, etc passive.
- Metal + $HNO_3 \longrightarrow$ Metal nitrate + [H]
- Causes nitration of organic compounds.

Phosphorus (P_4)



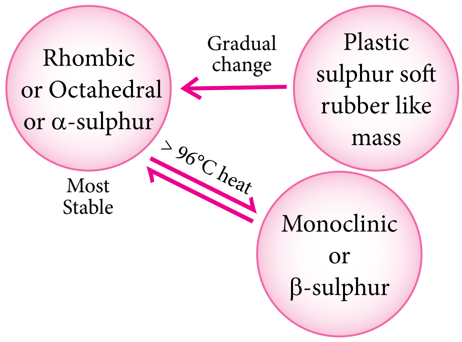
Oxygen	Ozone
$:\ddot{O}=\ddot{O}:$	
Laboratory Preparation	
$2KClO_3 \xrightarrow{420\text{ K}} 2KCl + 3O_2$	$3O_2 \rightleftharpoons 2O_3$ – energy 5-10% ozone mixture is obtained, known as ozonised oxygen.
Properties	
$2H_2 + O_2 \xrightarrow[\text{or electric discharge}]{1073\text{ K}} 2H_2O$ $2NO + O_2 \longrightarrow 2NO_2$ $P_4 + 5O_2 \longrightarrow P_4O_{10}$ $4Al + 3O_2 \longrightarrow 2Al_2O_3$	$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O; E° = +2.07$ V $2HCl + O_3 \longrightarrow H_2O + Cl_2 + O_2$ $PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$ $I_2 + H_2O + 5O_3 \longrightarrow 2HIO_3 + 5O_2$ Coloured substance + [O] $\longrightarrow$ Colourless substance (Bleaching action)

INFO SHOTS

van der Waals' forces !

Very weak van der Waals' forces between individual atoms are measured for the first time. Individual noble gas atoms were fixed within a molecular network and the interactions with a single xenon atom were determined that was positioned at the tip of an atomic force microscope. As expected, the forces varied according to the distance between the two atoms, but in some cases, the forces were several times larger than theoretically calculated.

Allotropic Forms of Sulphur



Sulphuric Acid

- **Lead chamber process :**

  $2SO_2 + O_2 + 2H_2O \xrightarrow[\text{(Catalyst)}]{NO} 2H_2SO_4$

- **Contact process :**

  $2SO_2 + O_3 \xrightleftharpoons{\text{Catalyst}} 2SO_3$

  $H_2SO_4 + SO_3 \longrightarrow \underset{\text{(oleum)}}{H_2S_2O_7} \xrightarrow{+H_2O} 2H_2SO_4$

- **Properties**
  - **As oxidising agent (due to nascent O) :**

    $H_2SO_4 \xrightleftharpoons{444°C} H_2O + SO_2 + [O]$

    $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

    $S_8 + 16H_2SO_4 \longrightarrow 24SO_2 + 16H_2O$

    $P_4 + 10H_2SO_4 \longrightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$

    $2KI + 2H_2SO_4 \longrightarrow K_2SO_4 + SO_2 + I_2 + 2H_2O$
  - **As dibasic acid :**

    $Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$

    $2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$

Bleaching Powder ($CaOCl_2 \cdot H_2O$)

- **Preparation :**

  $\underset{\text{Dry slaked lime}}{Ca(OH)_2} + Cl_2 \longrightarrow CaOCl_2 + H_2O$

  Preparation is carried out in Hasenclever's plant and Beckmann's plant.

- **Properties**

  $6CaOCl_2 \xrightarrow{\text{On long standing}} Ca(ClO_3)_2 + 5CaCl_2$

- **Oxidising properties :**

  $CaOCl_2 + H_2S \longrightarrow CaCl_2 + H_2O + S$

  $3CaOCl_2 + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2$

- **Bleaching action :**

  Coloured matter + [O] $\longrightarrow$ Colourless product

Interhalogen Compounds

Type XX'_1 (Linear shape)	Type XX'_3 (T-shape)	Type XX'_5 (Square pyramidal shape)	Type XX'_7 (Pentagonal bipyramidal shape)
ClF	ClF_3	ClF_5	
BrF, BrCl	BrF_3	BrF_5	
ICl, IBr, IF	ICl_3, IF_3	IF_5	IF_7

Compounds of Xenon

Molecule	Electron pairs	Hybridisation	Shape
XeF_2	5	sp^3d	Linear
XeF_4	6	sp^3d^2	Square planar
XeF_6	7	sp^3d^3	Distorted octahedral
$XeOF_2$	5	sp^3d	T-shape
$XeOF_4$	6	sp^3d^2	Square pyramidal
XeO_3	4	sp^3	Pyramidal
XeO_2F_2	5	sp^3d	See-saw
XeO_4	4	sp^3	Tetrahedral

SPEED PRACTICE

1. From the following information,
$X + H_2SO_4 \longrightarrow Y$ (a colourless and irritating gas)
$Y + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ green coloured solution
Identify the pair X and Y.
(a) Cl^-, HCl (b) SO_3^{2-}, SO_2
(c) S^{2-}, H_2S (d) CO_3^{2-}, CO_2

2. In the commercial electrochemical process for aluminium extraction, the electrolyte used is
(a) $Al(OH)_3$ in NaOH solution
(b) an aqueous solution of $Al_2(SO_4)_3$
(c) a molten mixture of Al_2O_3 and Na_3AlF_6
(d) a molten mixture of AlO(OH) and $Al(OH)_3$

3. Which of the following is correct statement?
(a) Phosphates have no biological significance in humans.
(b) Between nitrates and phosphates, phosphates are less abundant in earth's crust.
(c) Between nitrates and phosphates, nitrates are less abundant in earth's crust.
(d) Oxidation of nitrates is possible in soil.

4. Composition of azurite mineral is
(a) $CuCO_3 \cdot CuO$
(b) $Cu(HCO_3)_2 \cdot Cu(OH)_2$
(c) $2CuCO_3 \cdot Cu(OH)_2$
(d) $CuCO_3 \cdot 2Cu(OH)_2$

5. The number of S $=$ O and S — OH bonds present in peroxodisulphuric acid and pyrosulphuric acid are respectively
(a) (4 and 2) and (4 and 2)
(b) (2 and 4) and (2 and 4)
(c) (4 and 2) and (2 and 4)
(d) (2 and 2) and (2 and 2)
(JEE Main Online 2017)

6. In the construction of aircrafts, an alloy, elektron is often used. Its composition is
(a) 15% Mg and 85% Al
(b) 95% Mg and 5% Zn
(c) 95% Mg and 5% Al
(d) 80% Al and 20% Zn

7. Which of the following is not correct?
(a) $3O_2 \underset{\text{discharge}}{\xrightarrow{\text{Silent electric}}} 2O_3$; $\Delta H = -284.5$ kJ mol^{-1}
(b) Ozone undergoes addition reaction with unsaturated carbon compounds.
(c) Sodium thiosulphate reacts with I_2 to form sodium tetrathionate and sodium iodide.
(d) Ozone oxidises lead sulphide to lead sulphate.

8. The process is used to remove reducible oxides from metals. Molten impure metal is stirred by a wooden rods. The hydrocarbon gases reduce the oxides. The process is called
(a) zone refining (b) cupellation
(c) poling (d) leaching.

9. Roasted copper pyrite on smelting with sand produces
(a) $FeSiO_3$ as fusible slag and Cu_2S as matte
(b) $CaSiO_3$ as infusible slag and Cu_2O as matte
(c) $Ca_3(PO_4)_2$ as fusible slag and Cu_2S as matte
(d) $Fe_3(PO_4)_2$ as infusible slag and Cu_2S as matte.

10. The correct statement(s) about the oxoacids, $HClO_4$ and HClO, is(are)
(a) the conjugate base of $HClO_4$ is weaker base than H_2O
(b) the central atom in both $HClO_4$ and HClO is sp^3 hybridized
(c) $HClO_4$ is formed in the reaction between Cl_2 and H_2O
(d) $HClO_4$ is more acidic than HClO because of the resonance stabilization of its anion.
(JEE Advanced 2017)

11. Hydrolysis of XeF_4 and CaNCN give respectively
(a) XeO_3 and $CaCO_3$ (b) XeO_2 and $CaCN_2$
(c) XeO_3 and $CaCN_2$ (d) $XeOF_2$ and $CaCO_3$

12. Xenon hexafluoride reacts with potassium fluoride to yield
(a) $[XeF_4]^{2+} [KF_3]^{2-}$ (b) XeF_4
(c) $[XeF_5]^+ [KF_2]^-$ (d) $K^+[XeF_7]^-$

13. Pb, which is present as impurity in silver, is removed by
(a) Parke's process
(b) Pattinson process
(c) cupellation
(d) addition of Zn in molten silver.

14. Which of the following diagrams is correctly related to the extraction of Mg from sea water?
(a) Sea water $\xrightarrow{Na_2CO_3}$ $MgCO_3$ $\xrightarrow{\text{Calcination}}$ MgO $\xrightarrow[\text{reduction}]{\text{Carbon}}$ Mg
(b) Sea water $\xrightarrow[\text{water}]{\text{lime}}$ $Mg(OH)_2$ $\xrightarrow{HCl_{(aq.)}}$ $MgCl_2.6H_2O$ $\xrightarrow[\text{With excess of dry } HCl_{(g)}]{\Delta}$ $MgCl_2$ Anhyd. $\xrightarrow[\text{in molted condition}]{\text{Electrolysis}}$ Mg
(c) Sea water $\xrightarrow{\text{drying}}$ Sea salt $\xrightarrow{\text{Electrolysis}}$ Mg
(d) Sea water $\xrightarrow{Ca(OH)_2}$ $Mg(OH)_2$ $\xrightarrow{HCl_{(aq.)}}$ $MgCl_2$ Solution $\xrightarrow[\text{in aq. solution}]{\text{Electrolysis}}$ Mg

15. When copper is heated with conc. HNO_3 it produces
(a) $Cu(NO_3)_2$, NO and NO_2
(b) $Cu(NO_3)_2$ and N_2O
(c) $Cu(NO_3)_2$ and NO_2
(d) $Cu(NO_3)_2$ and NO **(NEET 2016)**

16. Out of $H_2S_2O_3$, $H_2S_2O_6$, H_2SO_5 and $H_2S_2O_8$ peroxy acids are
(a) $H_2S_2O_3$, $H_2S_4O_6$ (b) $H_2S_4O_6$, H_2SO_5
(c) H_2SO_5, $H_2S_2O_8$ (d) $H_2S_2O_3$ and $H_2S_2O_8$

17. The process of pickling is to
(a) cover metal surface with a less reactive metal
(b) electroplate a metal with a non-metal
(c) cool a red hot steel by dipping it in oil
(d) remove layers of basic oxides from metal surface before electroplating.

18. Which series of reactions correctly represents chemical relations related to iron and its compound?
(a) Fe $\xrightarrow{O_2,\ \text{heat}}$ Fe_3O_4 $\xrightarrow{CO,\ 600°C}$ FeO $\xrightarrow{CO,\ 700°C}$ Fe
(b) Fe $\xrightarrow{\text{dil. } H_2SO_4}$ $FeSO_4$ $\xrightarrow{H_2SO_4,\ O_2}$ $Fe_2(SO_4)_3$ $\xrightarrow{\text{heat}}$ Fe
(c) Fe $\xrightarrow{O_2,\ \text{heat}}$ FeO $\xrightarrow{\text{dil. } H_2SO_4}$ $FeSO_4$ $\xrightarrow{\text{heat}}$ Fe
(d) Fe $\xrightarrow{Cl_2,\ \text{heat}}$ $FeCl_3$ $\xrightarrow{\text{heat, air}}$ $FeCl_2$ $\xrightarrow{Zn}$ Fe
(JEE Main 2014)

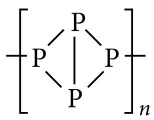
19. Pitch blende is
(a) ore of Ti (b) ore of U
(c) ore of W (d) ore of B.

20. Which is incorrectly matched?
(a) $CsBr_3 \rightleftharpoons Cs^+ + Br_3^-$
(b) $I_4O_9 \rightleftharpoons I^{3+} + 3IO_3^-$
(c) $AgBrO_3 \rightleftharpoons Ag^+ + BrO_3^-$
(d) $I_2O_4 \rightleftharpoons IO_2^+ + IO_2^-$

21. The chemical composition of slag formed during the smelting process in the extraction of copper is
(a) $Cu_2O + FeS$ (b) $FeSiO_3$
(c) $CuFeS_2$ (d) $Cu_2S + FeO$

22. The non-metal that does not exhibit positive oxidation state is
(a) chlorine (b) iodine
(c) fluorine (d) oxygen.
(JEE Main Online 2016)

23. Which of the following allotropic forms of phosphorus contain given structure?



(a) White phosphorus (b) Red phosphorus
(c) Black phosphorus (d) Yellow phosphorus

24. Which of the following is correct?
(a) Superphosphate is $[3Ca(H_2PO_4)_2 + 7CaSO_4]$.
(b) Triple superphosphate is $Ca(H_2PO_4)_2$.
(c) Both (a) and (b)
(d) None of these

25. In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with
(a) carbon monoxide (b) copper (I) sulphide
(c) sulphur dioxide (d) iron (II) sulphide.
(NEET 2015)

MPP-5 CLASS XI ANSWER KEY

1.	(a)	2.	(a)	3.	(d)	4.	(a)	5.	(c)
6.	(d)	7.	(b)	8.	(c)	9.	(d)	10.	(b)
11.	(d)	12.	(a)	13.	(a)	14.	(a)	15.	(c)
16.	(b)	17.	(a)	18.	(b)	19.	(b)	20.	(a,d)
21.	(a,b,c,d)	22.	(a,b,c)	23.	(a,b)	24.	(4)	25.	(7)
26.	(3)	27.	(d)	28.	(a)	29.	(b)	30.	(b)

26. When an inorganic compound reacts with SO_2 in aqueous medium produces (A). (A) on reaction with Na_2CO_3 gives the compound (B) which with sulphur gives a substance (C) used in photography. The compound (C) is
(a) $Na_2S_2O_3$ (b) Na_2SO_4
(c) Na_2S (d) $Na_2S_2O_7$

27. In which pair of ions both the species contain S — S bond?
(a) $S_4O_6^{2-}, S_2O_3^{2-}$ (b) $S_2O_7^{2-}, S_2O_8^{2-}$
(c) $S_4O_6^{2-}, S_2O_7^{2-}$ (d) $S_2O_7^{2-}, S_2O_3^{2-}$
(NEET 2017)

28. Compounds formed when the noble gases get entrapped in the cavities of crystal lattices of certain organic and inorganic compounds are known as
(a) interstitial compounds
(b) clathrates
(c) hydrates (d) picrates.

29. Cassiterite is concentrated by
(a) levigation
(b) electromagnetic separation
(c) floatation
(d) liquefaction.

30. In which of the following reactions HNO_2 acts as an oxidising agent?
(a) $MnO_4^- + NO_2^- + H^+ \longrightarrow Mn^{2+} + NO_3^- + H_2O$
(b) $KI + H_2SO_4 + HNO_2 \longrightarrow K_2SO_4 + NO + I_2 + H_2O$
(c) $Cl_2 + HNO_2 \longrightarrow HCl + NO_2$
(d) $O_3 + NO_2^- + H^+ \longrightarrow O_2 + NO_3^- + H_2O$

SOLUTIONS

1. (b): $\underset{(X)}{SO_3^{2-}} + 2H^+ \longrightarrow \underset{(Y)}{SO_2} + H_2O$

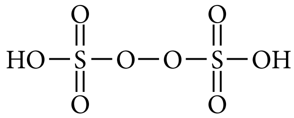
$3SO_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{Green coloured solution}}{Cr_2(SO_4)_3} + H_2O$

2. (c) : The electrolysis of pure alumina faces some difficulties. Pure alumina is a bad conductor of electricity. The fusion temperature of pure alumina is about 2000°C. At this temperature, when electrolysis is carried out on the fused mass, the metal formed vaporises, as the boiling point of aluminium is 1800°C. These difficulties are overcome by using a mixture containing alumina, cryolite (Na_3AlF_6), and fluorspar (CaF_2).

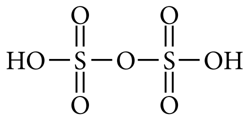
3. (c) : Between nitrates and phosphates, nitrates are more soluble in water and hence, are less abundant in earth's crust.

4. (c) : Azurite is a basic copper carbonate ore having composition $2CuCO_3 \cdot Cu(OH)_2$.

5. (a) : Peroxodisulphuric acid :

$H_2S_2O_8$: 

No. of S = O bonds = 4
No. of S — OH bonds = 2
Pyrosulphuric acid :

$H_2S_2O_7$: 

No. of S = O bonds = 4 ; No. of S — OH bonds = 2

6. (c) : Elektron is magnesium alloy containing 0% to 9.5% of some of the following elements in varying proportion aluminium (< 9.5%), yttrium (5.25%), silver (2.5%), etc.

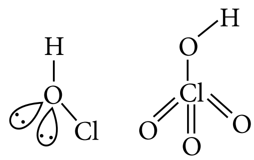
7. (a) : The given reaction is endothermic.

$3O_2 \xrightarrow[\text{discharge}]{\text{Silent electric}} 2O_3$; $\Delta H = +142$ kJ mol^{-1}

8. (c)

9. (a) : During smelting, silica combines with FeO to form fusible $FeSiO_3$ slag and Cu_2S as matte.

10. (a,b,d) : Structures of HClO and $HClO_4$ are :



(a) $HClO_4$ is a stronger acid than H_3O^+. Therefore, conjugate base of $HClO_4$, *i.e.*, ClO_4^-, is weaker base than H_2O.
(b) The hybridisation of central atom in both HClO and $HClO_4$ is sp^3.
(c) Reaction of Cl_2 with water forms HOCl which decomposes to give nascent oxygen.
$Cl_2 + H_2O \rightarrow [HCl + HOCl] \rightarrow 2HCl + [O]$
(d) $HClO_4$ is more acidic than HClO as ClO_4^- is more stable than ClO^- due to resonance.

11. (a) : $6XeF_4 + 12H_2O \xrightarrow[\text{hydrolysis}]{\text{Partial}} 2XeO_3 + 24HF + 4Xe + 3O_2$

$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$

12. (d): XeF_6 behaves as F^- acceptor to form fluoro-anions.
$XeF_6 + KF \longrightarrow K^+[XeF_7]^-$

13. (c)

14. (b): Sea water contains Mg^{2+} ions.

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2$$

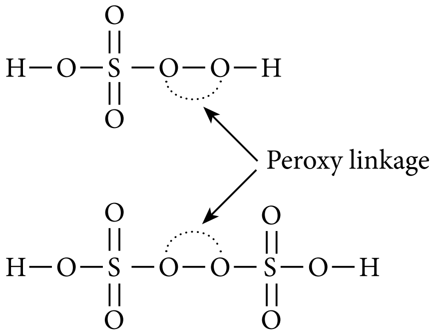
$$Mg(OH)_2 \xrightarrow{HCl_{(aq.)}} MgCl_2.6H_2O$$

$$MgCl_2.6H_2O \xrightarrow[\Delta]{\text{Dry } HCl_{(g)}} \underset{\text{(Anhydrous)}}{MgCl_2}$$

$$\underset{\text{(Molten salt)}}{MgCl_2} \xrightarrow{\text{Electrolysis}} \underset{\text{(At cathode)}}{Mg} + \underset{\text{(At anode)}}{Cl_2}$$

15. (c) : $Cu + 4HNO_3(conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

16. (c) :



17. (d)

18. (a) : Combustion of Fe to give Fe_3O_4 which upon reduction with CO first gives FeO and finally Fe. Option (b) and (c) are wrong because $FeSO_4$ and $Fe_2(SO_4)_3$ on heating gives Fe_2O_3, SO_2, SO_3 and not Fe.

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$$

$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_3 + SO_2$$

Option (d) is wrong because in presence of air, reduction of $FeCl_3$ to $FeCl_2$ cannot occur.

19. (b)

20. (d): $I_2O_4 \rightleftharpoons I^+ + IO_4^-$

21. (b): When smelting is done in the blast furnace, most of the ferrous oxide is converted to ferric oxide. With silica, it forms ferrous silicate, which is the slag.

$$\underset{\text{(Gangue)}}{FeO} + \underset{\text{(Flux)}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

22. (c) : Fluorine is the most electronegative element and it shows only –1 oxidation state.

23. (b): Polymeric form of $\left(P_4 \right)_n$ is red phosphorus.

24. (c)

25. (b): $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

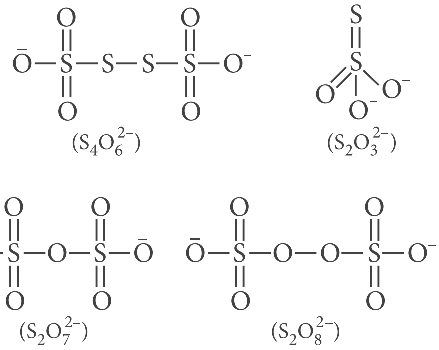
It is an example of auto-reduction.

26. (a) : $Na_2CO_3 + 2SO_2 + H_2O \longrightarrow \underset{(A)}{2NaHSO_3} + CO_2$

$$2NaHSO_3 + Na_2CO_3 \longrightarrow \underset{(B)}{2Na_2SO_3} + H_2O + CO_2$$

$$Na_2SO_3 + S \longrightarrow \underset{(C)}{Na_2S_2O_3}$$

27. (a):



28. (b)

29. (b): Cassiterite is tinstone (SnO_2) which is non-magnetic and contains wolframite, $FeWO_4$ (magnetic) impurities. These are separated by electromagnetic separation.

30. (b): HNO_2 oxidises KI to iodine (I_2).

EXAMINER'S MIND CLASS XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

THE *p*-BLOCK ELEMENTS (GROUP 15 TO 18)

SECTION - I

Only One Option Correct Type

1. Under normal conditions, which of the following hydrides is non-combustible?
(a) NH_3 (b) PH_3 (c) AsH_3 (d) SbH_3

2. Aqueous solutions of hydrogen sulphide and sulphur dioxide when mixed together, yield
(a) sulphur and water
(b) sulphur trioxide and water
(c) hydrogen peroxide and sulphur
(d) hydrogen and sulphurous acid.

3. Which among the following factors is most important in making fluorine the strongest oxidising agent?
(a) Electron affinity (b) Ionisation energy
(c) Hydration energy
(d) Bond dissociation energy

4. The heat of vaporisation, polarisation and solubility in water of noble gases are in the order
(a) He< Ne < Ar < Kr < Xe
(b) Xe < Kr < Ar < Ne < He
(c) He < Ne < Ar < Xe < Kr
(d) He < Ne ≈ Ar < Kr ≈Xe

5. Sodium hydroxide solution reacts with phosphorus to give phosphine. To bring about this reaction, we need
(a) white phosphorus and dil. NaOH
(b) white phosphorus and conc. NaOH
(c) red phosphorus and dil. NaOH
(d) red phosphorus and conc. NaOH.

6. Which of the following properties of H_2SO_4 in respective reaction is wrong?
(a) $\begin{array}{l}COOH\\ |\\ COOH\end{array} \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$;
H_2SO_4 acts as dehydrating agent.
(b) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$;
H_2SO_4 acts as oxidising agent.
(c) $Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$;
H_2SO_4 acts as an acid.
(d) $2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 + Br_2$;
H_2SO_4 acts as reducing agent.

7. A black compound of manganese reacts with a halogen acid to give greenish yellow gas. When excess of this gas reacts with NH_3 and unstable trihalide is formed. In this process, the oxidation state of nitrogen changes from
(a) −3 to +3 (b) −3 to 0
(c) −3 to +5 (d) 0 to −3

8. The stability of interhalogen compounds follows the order
(a) $IF_3 > BrF_3 > ClF_3$ (b) $BrF_3 > IF_3 > ClF_3$
(c) $ClF_3 > BrF_3 > IF_3$ (d) $ClF_3 > IF_3 > BrF_3$

9. The reaction between NH_2^- and N_2O gives
(a) NO (b) N_2O_5
(c) NH_2NH_2 (d) N_3^-

10. Which of the following statements regarding sulphur is incorrect?
(a) S_2 molecule is paramagnetic.
(b) The vapour at 200°C consists mostly of S_8 rings.
(c) At 600°C the gas mainly consists of S_2 molecules.
(d) The oxidation state of sulphur is never less than +4 in its compounds.

SECTION - II

More than One Options Correct Type

11. Which of the following statements are incorrect?
(a) Dry slaked lime reacts with Cl_2 to give calcium chlorate.
(b) With excess chlorine ammonia forms nitrogen trichloride.
(c) Sulphur reacts with Cl_2 to give SCl_4.
(d) With hot and conc. NaOH, Cl_2 gives sodium chlorate.

12. Which statements regarding argon in solid state are correct?
(a) Its atoms form a covalent network.
(b) The forces between the molecules are weak van der Waals' forces.
(c) Its molecules are monoatomic.
(d) It is good conductor of electricity.

13. Ammonia on reaction with hypochlorite anion can form
(a) NO (b) NH_4Cl (c) N_2H_4 (d) HNO_2

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

Industrially sulphuric acid is produced by the following steps :

Step I : $S + O_2 \xrightarrow{\Delta} SO_2$

Step II : $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

Step III : $SO_3 + H_2O \longrightarrow H_2SO_4$

Since the reaction between SO_3 and H_2O is violent, therefore, SO_3 is passed into 98% H_2SO_4 to produce oleum ($H_2S_2O_7$).

14. Pure H_2SO_4 does not react with metal because
(a) pure H_2SO_4 does not contain any water
(b) pure H_2SO_4 acts as an oxidising agent
(c) pure H_2SO_4 is strongly H-bonded
(d) pure H_2SO_4 does not contain any SO_3.

15. $H_2SO_4 + PCl_5 \longrightarrow (X) \xrightarrow{H_2O}$ two strong acids
Therefore (X) is
(a) SO_2Cl_2 (b) SOCl
(c) $ClSO_3H$ (d) $POCl_3$

Paragraph for Questions 16 and 17

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6. XeF_4 reacts violently with water to give XeO_3. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

16. The structure of XeO_3 is
(a) linear (b) planar
(c) pyramidal (d) T-shaped.

17. XeF_4 and XeF_6 are expected to be
(a) oxidising (b) reducing
(c) unreactive (d) strongly basic.

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

List I	List II
(P) P_4O_6	(i) White crystalline solid
(Q) P_4O_{10}	(ii) Waxy solid with garlic smell
(R) N_2O_3	(iii) Blue coloured liquid
(S) N_2O_5	(iv) Coordinate bonds

(a) (P-i,); (Q-ii, iv); (R-iii); (S-iv)
(b) (P-ii); (Q-i, iv); (R-iii); (S-i, iv)
(c) (P-i); (Q-i, iii); (R-iv); (S-i, ii, iii)
(d) (P-ii); (Q-i, iii); (R-iv); (S-i)

19 . Match the List I with List II and select the correct answer using the codes given below the lists :

List I	List II
(A) Helium	(p) Ionisation energy comparable to O_2
(B) Argon	(q) Provides inert atmosphere in metallurgy
(C) Neon	(r) Cryogenic
(D) Xenon	(s) For advertising sign

(a) A-q; B-s; C-p; D-r (b) A-q; B-p; C-s; D-r
(c) A-r; B-q; C-s; D-p (d) A-r; B-s; C-q; D-p

SECTION - V

Assertion Reason Type

20. **Assertion :** H_3PO_3 and H_3PO_4 are tribasic acids as they contain three hydrogen atoms each.

Reason : Both H_3PO_3 and H_3PO_4 are reducing in nature.

21. **Assertion :** Reaction of SO_2 and H_2S in the presence of Fe_2O_3 catalyst gives elemental sulphur.

Reason : In this reaction H_2S is acting as a reducing agent.

22. **Assertion :** $HClO_4$ is less acidic than $HBrO_4$.

Reason : $HClO_4$ ionises less in water than $HBrO_4$.

SECTION - VI

Integer Value Correct Type

23. What is the oxidation state of chlorine in $HClO_4$?

24. Number of P—OH bonds present in pyrophosphoric acid is

25. Amongst the following, the maximum number of isoelectronic molecules/ions are

XeO_3, BrO_3^-, ClF, XeF_2, OF_2, XeF_4, ICl_4^-, ClO^-, IBr_2^-

ALCOHOLS, PHENOLS AND ETHERS

SECTION - I

Only One Option Correct Type

1. When 2,3-dimethyl-2-butanol undergoes acid catalysed dehydration the minor product is

(a) 2, 3-dimethyl-1-butene

(b) 2, 3-dimethyl-2-butene

(c) 3, 3-dimethyl-1-butene

(d) none of these.

2. What is the function of diethyl ether in Grignard reagent preparation?

1. To act as catalyst
2. To act as solvent
3. To provide lone pair of electrons for coordination
4. To act as an acid

(a) 1,2 (b) 2,3 (c) 3,4 (d) 2,4

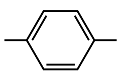
3. Which of the following is not true in case of reaction with heated copper at 300°C?

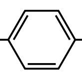
(a) Phenol $\longrightarrow$ Benzyl alcochol

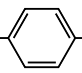
(b) Primary alcohol $\longrightarrow$ Aldehyde

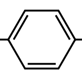
(c) Secondary alcohol $\longrightarrow$ Ketone

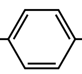
(d) Tertiary alcohol $\longrightarrow$ Olefin

4. The reaction of $CH_3CH{=}CH$  OH with HBr gives

(a) $CH_3CHBrCH_2$–  –OH

(b) CH_3CH_2CHBr–  –OH

(c) $CH_3CHBrCH_2$–  –Br

(d) CH_3CH_2CHBr–  –Br

5. For which of the following parameters the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have same values? (Assume ideal behaviour)

(a) Vapour pressure at the same temperature

(b) Heat of vaporisation

(c) Gaseous densities at the same temperature and pressure

(d) Boiling points

6. Which of the following statements are correct?

I. Glycerol on reaction with oxalic acid at 110°C (383 K) and followed by hydrolysis gives formic acid and glycerol.

II. Glycerol on reaction with oxalic acid at 230°C (503 K) and followed by heating gives allyl alcohol.

III. Glycerol on oxidation with dil. HNO_3 gives a mixture of glyceric and tartonic acid.

IV. Glycerol on oxidation with conc. HNO_3 gives glyceric acid.

(a) I and II (b) I and III

(c) III and IV (d) I, II, III, IV

7. Isopropyl benzene is oxidised in the presence of air to give a compound '*A*'. When compound '*A*' is treated with dilute mineral acid, the aromatic product formed is

(a) phenol (b) benzene

(c) benzaldehyde (d) acetophenone.

8. Intramolecular rearrangement of phenyl acetate to give *o*- and *p*-hydroxyacetophenone in the presence of anhydrous $AlCl_3$ is known as

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

(c) Fries rearrangement

(d) Claisen rearrangement.

9. Identify X in the following sequence :

$$\underset{(X)}{C_3H_8O} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} C_3H_6O \xrightarrow[I_2+NaOH]{\text{warm}} CHI_3$$

(a) $CH_3CH_2CH_2OH$ (b) $CH_3CHOHCH_3$
(c) $CH_3OCH_2CH_3$ (d) CH_3CH_2CHO

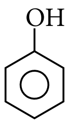
10. What amount of bromine will be required to convert 2 g of phenol into 2, 4, 6-tribromophenol?
(a) 4.00 g (b) 6.00 g
(c) 10.08 g (d) 20.44 g

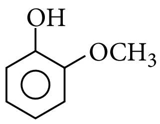
SECTION - II

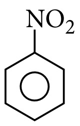
More than One Options Correct Type

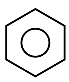
11. Phenol is less acidic than
(a) acetic acid (b) *p*-methoxyphenol
(c) *p*-nitrophenol (d) ethanol.

12. Which of the following compounds may undergo Reimer-Tiemann reaction?

(a) 

(b) 

(c) 

(d) 

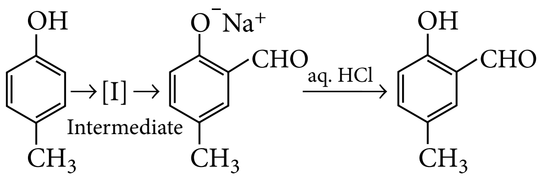
13. Which of the following compounds will give a yellow precipitate with iodine and alkali?
(a) Acetophenone (b) Methyl acetate
(c) Acetamide (d) 2-Hydroxypropane

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

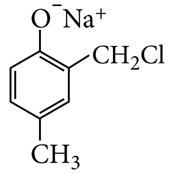
Reimer-Tiemann reaction introduces aldehyde group on to the aromatic ring of phenol, *ortho* to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of a substituted salicylaldehydes as depicted below.

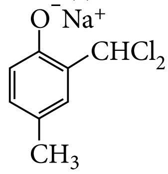


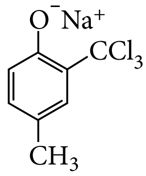
(I) (II) (III)

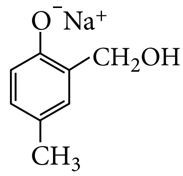
14. Which one of the following reagents is used in the above reaction?
(a) aq. NaOH + CH_3Cl
(b) aq. NaOH + CH_2Cl_2
(c) aq. NaOH + $CHCl_3$
(d) aq. NaOH + CCl_4

15. The structure of the intermediate (I) is

(a) 

(b) 

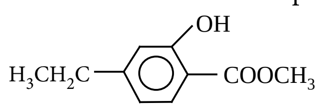
(c) 

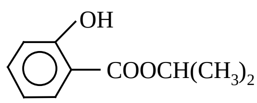
(d) 

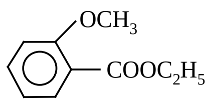
Paragraph for Questions 16 and 17

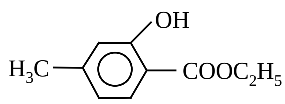
Compound (A), $C_{10}H_{12}O_3$ is insoluble in water, dil. HCl and dilute aq. $NaHCO_3$. It is however soluble in dilute NaOH. A solution of (A) in dilute NaOH was boiled and the distillate collected in a solution of NaOI, where a yellow precipitate was formed. The alkaline residue in the distillation flask was acidified with dil. H_2SO_4 to precipitate a solid (B), which was boiled, steam distilled and collected. The pure steam distilled product (B) was found to have the formula, $C_7H_6O_3$ and it was dissolved in aq. $NaHCO_3$ with effervescence.

16. The structural formula of compound (A) is

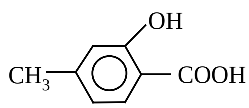
(a) 

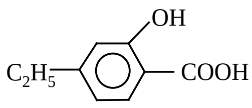
(b) 

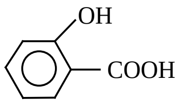
(c) 

(d) 

17. The structural formula of compound (B) is

(a) 

(b) 

(c) 

(d) none of these.

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

List I (Compounds)		List II (Methods to distinguish)
(P) Methanol and ethanol	1.	Lucas reagent
(Q) Phenol and cyclohexanol	2.	Sodium metal
(R) *n*-Butyl alcohol and *tert*-butyl alcohol	3.	Iodoform test
(S) Ethanol and diethyl ether	4.	Ferric chloride

	P	Q	R	S
(a)	2	4	1	3
(b)	4	1	2	3
(c)	1	2	3	4
(d)	3	4	1	2

19. Match the List I with List II and select the correct answer using the codes given below the lists :

List I (Reaction)		List II (Product)
(P) Reimer-Tiemann reaction	1.	Benzoquinone
(Q) Kolbe's reaction	2.	Salicylaldehyde
(R) Williamson synthesis	3.	Salicylic acid
(S) Oxidation of phenol	4.	Ether

	P	Q	R	S
(a)	3	4	2	1
(b)	3	4	1	2
(c)	4	3	1	2
(d)	2	3	4	1

SECTION - V

Assertion Reason Type

20. **Assertion :** Phenol is more reactive than benzene.
Reason: In case of phenol, the intermediate carbocation is more resonance stabilised.

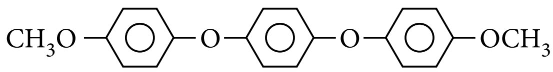
21. **Assertion :** The ease of dehydration of alcohols follows the order : Primary > Secondary > Tertiary.
Reason: Dehydration proceeds through the formation of oxonium ions.

22. **Assertion :** *tert*-Butyl methyl ether is not prepared by the reaction of *tert*-butyl bromide with sodium methoxide.
Reason : Sodium methoxide is a weak nucleophile.

SECTION - VI

Integer Value Correct Type

23. How many of structurally isomeric pentyl alcohols will give immediate turbidity in Lucas test?

24 

How many moles of HI consumed in above reaction?

25. How many of the following ethers cannot be prepared by Williamson's synthesis?
$CH_3OCH_2CH_3, C_6H_5OCH_3, C_6H_5OCH_2CH_3, (C_6H_5)_2O, (CH_3)_3COCH_3, (CH_3)_3COCH_2CH_3, (CH_3)_3COC(CH_3)_3, (C_2H_5)_2O, C_6H_5CH_2OC_6H_5$

SOLUTIONS

THE *p*-BLOCK ELEMENTS (GROUP 15 TO 18)

1. **(a)**
2. **(a) :** $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$
3. **(c) :** Although both hydration energy and bond dissociation energy make F_2 a strong oxidising agent but the effect of hydration energy is more important.
4. **(a)**
5. **(a) :** $P_4 + \underset{\text{Caustic soda}}{3NaOH} + 3H_2O \longrightarrow \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3\uparrow}$
6. **(d):** Br^- has been changed to Br_2. H_2SO_4 is acting as an oxidising agent.
7. **(a) :** $MnO_2 + 4HCl \longrightarrow MnCl_2 + \underset{\text{Greenish yellow}}{Cl_2} + 2H_2O$

$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$
Oxidation state of N in $NH_3(-3)$ and in $NCl_3(+3)$.

8. **(a) :** The stability of interhalogens increases as the size difference and polarity of bond increases. Thus, the correct order of stability is $IF_3 > BrF_3 > ClF_3$.

9. **(d) :** $NH_2^- + N_2O \longrightarrow N_3^- + H_2O$

10. **(d) :** The oxidation state of sulphur in its compounds varies from −2 to +6.

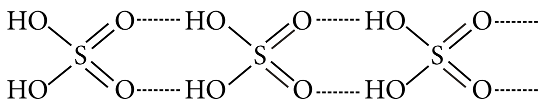
11. **(a,c) :** If chlorine is passed through dry slaked lime, bleaching powder is produced.
$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{Ca(OCl)Cl} + H_2O$
$S_8 + 4Cl_2 \longrightarrow \underset{\text{Sulphur monochloride}}{4S_2Cl_2}$

12. **(b,c)**

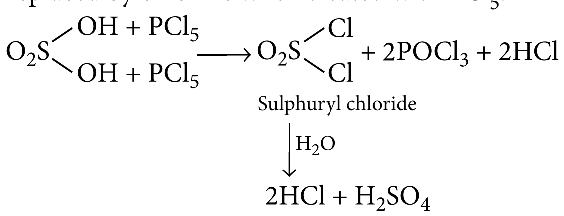
13. **(b,c) :** $NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$
$\underset{\text{Chloramine}}{NH_2Cl} + NH_3 \longrightarrow \underset{\text{Hydrazine}}{NH_2NH_2} + HCl$
$NaOH + HCl \longrightarrow NaCl + H_2O$

$2NH_3 + NaOCl \longrightarrow NH_2NH_2 + NaCl + H_2O$
Hydrazine produced may be decomposed by chloramine to N_2 and NH_4Cl.
$2NH_2Cl + N_2H_4 \longrightarrow 2NH_4Cl + N_2$

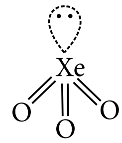
14. **(c) :** Pure H_2SO_4 does not act as oxidising agent, because its molecules are associated due to strong hydrogen bonds.



15. **(a) :** Two hydroxyl groups of sulphuric acid can be replaced by chlorine when treated with PCl_5.



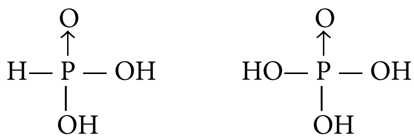
16. **(c) :** In XeO_3 there are total of 4 electron pairs around central atom. Out of which 3 are bonding electron pairs and one is non-bonding electron pair. Thus, it has sp^3 hybridisation and pyramidal shape.



17. **(a) :** All the xenon fluorides are strongly oxidising.

18. **(b)** 19. **(c)**

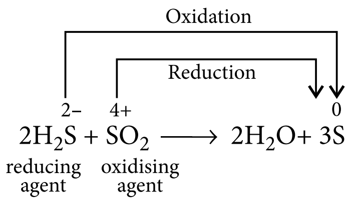
20. **(d) :**



H_3PO_3 (Dibasic) H_3PO_4 (Tribasic)

H_3PO_3 is reducing in nature but H_3PO_4 is not a reducing agent as in H_3PO_4, phosphorus is in +5 oxidation state.

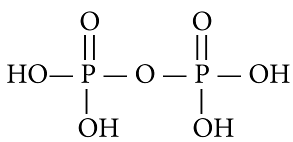
21. **(b) :**



22. **(d)**

23. **(7) :** The oxidation state of Cl in $HClO_4$ is +7.

24. **(4) :**

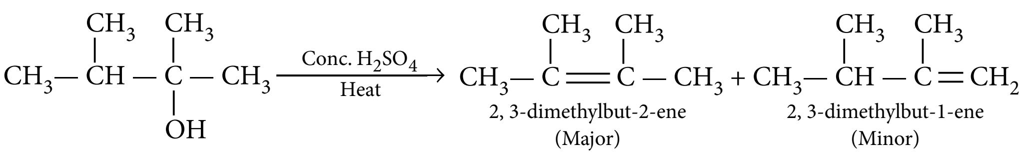


4(P—O—H) bonds are present in pyrophosphoric acid.

25. **(3) :** ClF (17 + 9 = 26), OF_2(8 + 2 × 9 = 26), ClO^-(17 + 8 + 1 = 26)

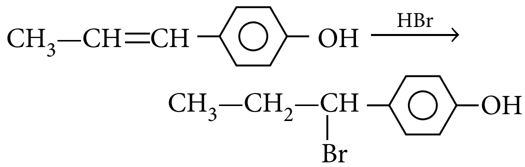
ALCOHOLS, PHENOLS AND ETHERS

1. **(a) :**



2. **(b)**

3. **(a) :** Phenol does not react with copper at 300°C.

4. (b): 

5. (c) : As C_2H_5OH and CH_3OCH_3 are isomers, they have the same molecular mass and have same values of gaseous densities at the same temperature and pressure.

6. (d)

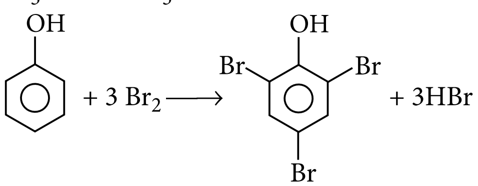
7. (a) :

$$\underset{\text{Isopropyl benzene}}{C_6H_5CH(CH_3)_2} \xrightarrow[\text{oxidation}]{\text{Aerial}} \underset{\text{Cumene hydroperoxide }(A)}{C_6H_5-C(CH_3)_2-OOH}$$

$$\xrightarrow{H^+/H_2O} \underset{\substack{\text{Phenol}\\ \text{(aromatic product)}}}{C_6H_5OH} + \underset{\substack{\text{Acetone}\\ \text{(aliphatic product)}}}{(CH_3)_2C{=}O}$$

8. (c)

9. (b): Since C_3H_6O on treatment with I_2 + NaOH gives CHI_3, therefore, C_3H_6O must be a methyl ketone, *i.e.* CH_3COCH_3. If this is so then, *X* must be $CH_3CHOHCH_3$.

10. (c): 

2,4,6-tribromophenol

94 grams of phenol requires bromine = 474 g

∴ 2 grams of phenol would require amount of bromine $= \frac{474}{94} \times 2 = 10.08$ g

11. (a,c) **12. (a,b)**

13. (a,d) : Compounds which contain CH_3CO- or CH_3CHOH- group attached to C or H on treatment with I_2 and alkali give yellow ppt. of iodoform.

$\boxed{CH_3-CO}-C_6H_5$ Acetophenone

$\boxed{CH_3-CO}-OCH_3$ Methyl acetate

$\boxed{CH_3-CO}-NH_2$ Acetamide

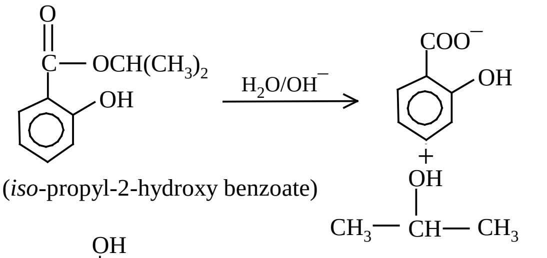
$\boxed{CH_3-CHOH}-CH_3$ 2-Hydroxypropane

Thus, acetophenone and 2-hydroxypropane give iodoform but acetamide and methyl acetate which although contain CH_3CO- group but that is not attached to C or H and hence, do not give iodoform.

14. (c) : For introduction of —CHO group, during Reimer-Tiemann reaction, a mixture of aq. NaOH + $CHCl_3$ is used.

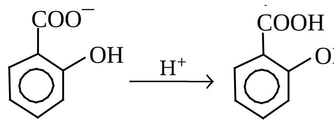
15. (b)

16. (b):



A (*iso*-propyl-2-hydroxy benzoate)

$$CH_3-CH(OH)-CH_3 \xrightarrow{I_2/\overline{O}H} \underset{\substack{\text{yellow}\\ \text{ppt.}}}{CHI_3\downarrow} + CH_3COO^-$$

17. (c) : 

(*B*)

18. (d) **19. (d)** **20. (a)**

21. (d): The ease of dehydration of alcohols can be explained on the basis of stability of the intermediate carbocation. Greater the stability of the carbocation formed, greater will be the rate of reaction. The order of stability of carbocation formed is

$$(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+$$

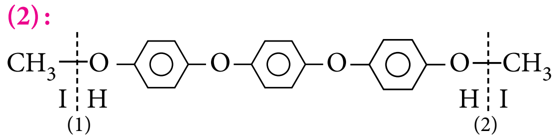
This is due to the electron releasing (+*I*) effect of the alkyl group. Therefore, the ease of dehydration of alcohols follows the order :

Tertiary > secondary > primary alcohols

22. (c) : Sodium ethoxide is a strong nucleophile.

23. (1): Only $H_3C-C(CH_3)(OH)-CH_2CH_3$, which is a tertiary alcohol, gives immediate turbidity with Lucas regent.

24. (2):



25. (2): Williamson's synthesis requires that the alkyl halide should be 1° and alkoxide ion may be 1°, 2° or 3°. Thus, two ethers which cannot be prepared by Williamson's synthesis are

$(C_6H_5)_2O$, $(CH_3)_3COC(CH_3)_3$ ◈◈

ACE YOUR WAY CBSE XII

Series 4

CHAPTERWISE PRACTICE PAPER : THE *d*- AND *f*-BLOCK ELEMENTS | COORDINATION COMPOUNDS

Time Allowed : 3 hours | Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carry 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Why do Zr and Hf exhibit similar properties?

2. Why is Ca-EDTA used for the treatment of lead poisoning?

3. What properties of tungsten make it suitable for use as filaments in light bulbs?

4. What is the coordination number of Fe in [Fe(EDTA)]?

5. State the kind of isomerism possible for the following :
(i) $[Cr(en)_3]^{3+}$
(ii) $[Cr(NH_3)_4(Cl)(Br)]Br$

6. What will be the correct order of absorption of wavelength of light in the visible region for the complexes $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$ and $[Co(H_2O)_6]^{3+}$?

7. Write the formula of the oxo-metal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

8. Specify the oxidation numbers of the metals in the following coordination entities :
(a) $[Co(H_2O)(CN)(en)_2]^{2+}$
(b) $[PtCl_4]^{2-}$
(c) $[Cr(NH_3)_3Cl_3]$ **(d)** $[CoBr_2(en)_2]^{+}$

9. Write the electronic configurations of the elements with the atomic numbers 61, 91, 101 and 109.

OR

Write the chemical equations for the reactions of $Cr_2O_7^{2-}$ with excess of (a) Fe^{2+} and (b) SO_3^{2-}.

10. Explain the crystal field splitting in square planar complexes.

11. How would you account for the following?
(i) The atomic radii of the third series of transition elements are virtually the same as those of the corresponding members of the second series.
(ii) The E^o value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple.
(iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride.

12. Calculate the crystal field stabilisation energy of a d^8 ion in a square planar field for both strong and weak field cases.

13. **(i)** Why are Sm^{2+}, Eu^{2+} and Yb^{2+} good reducing agents?

(ii) Can lanthanum (Z = 57) exhibit +4 oxidation state?

(iii) Why are +3 oxidation state of gadolinium (Z = 64) and lutetium (Z = 71) especially stable?

14. Name the following compounds :

(a) $[Co(en)_2(CN)_2]ClO_3$

(b) $K_4[Co(CN)_6]$

(c) $[Ni(NH_3)_6]_3\,[Co(NO_2)_6]_2$

15. Name the members of the lanthanoid series which exhibit + 4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configuration of these elements.

16. Write the correct formulae for the following coordination compounds :

(a) $CrCl_3{\cdot}6H_2O$ (violet, with 3 chloride ions/unit formula)

(b) $CrCl_3{\cdot}6H_2O$ (light green colour, with 2 chloride ions/unit formula)

(c) $CrCl_3{\cdot}6H_2O$ (dark green colour, with 1 chloride ion/unit formula)

OR

For the square coplanar complex $[Pt(NH_3)(NH_2OH)py(NO_2)]^+$, how many geometrical isomers are possible? Draw the structures of these isomers.

17. What are interstitial compounds? Explain them with reference to transition metals and mention their two important properties.

18. What can be inferred from the magnetic moment values of the following complex species?

	Example	Magnetic Moment (B.M.)
(i)	$K_4[Mn(CN)_6]$	1.7
(ii)	$[Fe(H_2O)_6]^{2+}$	4.9
(iii)	$K_2[MnCl_4]$	5.9

19. Decide giving reasons which one will exhibit the property indicated in the given pair.

(i) Sc^{3+} or Cr^{3+} : Paramagnetism

(ii) V or Mn : More number of oxidation states

(iii) V^{4+} or V^{5+} : Diamagnetism

20. Discuss briefly giving an example in each case the role of coordination compounds in

(i) biological systems **(ii)** medicinal chemistry

(iii) analytical chemistry.

21. Among lanthanoids, Ln(III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.

22. Draw geometrical isomers of the following :

(a) $[CoCl_2(en)_2]^+$ **(b)** $[Co(NH_3)_2Cl_2(en)]^+$

(c) $[Co(NH_3)Cl(en)_2]^{2+}$

23. Raman after passing M.Sc. in Chemistry joined a textile factory as a junior scientist. He came to know that factory is using chlorine based bleaching agents for bleaching of textiles. Raman suggested the chief production manager of the factory to use potassium permanganate instead of chlorine for bleaching purpose.

Now answer the following questions :

(i) Which property of $KMnO_4$ makes it a bleaching agent?

(ii) Write reduction half reaction of $KMnO_4$ in acidic medium.

(iii) Why is $KMnO_4$ better bleaching agent than chlorine?

(iv) What value is associated with the suggestion of Raman?

24. **(a)** Give the formula of each of the following coordination entities :

(i) Co^{3+} ion is bound to one Cl^-, one NH_3 molecule and two bidentate ethylene diamine (en) molecules.

(ii) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

Write the name and magnetic behaviour of each of the above coordination entities.

(b) Identify low spin and high spin complex out of these two.

OR

Indicate the oxidation state, electronic configuration, coordination number and magnetic moment for each of the following complexes.

(i) $K[Cr(H_2O)_2(C_2O_4)_2]{\cdot}3H_2O$

(ii) $[Co(NH_3)_5Cl]Cl_2$ **(iii)** $[CrCl_3(py)_3]$

(iv) $Cs[FeCl_4]$ **(v)** $K_4[Mn(CN)_6]$

25. **(i)** A black mineral (A) on treatment with dilute sodium cyanide solution in the presence of air gives a clear solution containing (B) and (C).

(ii) The solution of (B) on reaction with zinc gives precipitate of metal (D).

(iii) (D) dissolved in dil. HNO_3 and the resulting solution gives a white precipitate of (E) with dil. HCl.

(iv) (E) on fusion with sodium carbonate gives (D).
(v) (E) dissolved in aqueous solution of ammonia giving a colourless solution of (F).

Identify A to F and give chemical equations involved.

OR

(a) First ionisation energy of copper is higher than those of alkali metals, while second and third ionisation energies are lower. Explain.

(b) A mixed oxide of iron and chromium, $FeO \cdot Cr_2O_3$ is fused with sodium carbonate in the presence of air to form a yellow compound (A). On acidification, the compound (A) forms an orange coloured compound (B) which is a strong oxidising agent. Identify

(i) the compounds (A) and (B)

(ii) write balanced chemical equations for each step.

26. (a) Arrange the following complexes in the increasing order of conductivity of their solutions : $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$.

(b) Why do compounds having similar geometry have different magnetic moment?

(c) $CuSO_4 \cdot 5H_2O$ is blue in colour while $CuSO_4$ is colourless. Why?

OR

(a) Why are different colours observed in octahedral and tetrahedral complexes for the same metal and same ligands?

(b) What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex?

(c) $CoSO_4Cl \cdot 5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$.

Answer the following questions :

(i) Identify 'A' and 'B' and write their structural formulae.

(ii) Name the type of isomerism involved.

(iii) Give the IUPAC name of 'A' and 'B'.

SOLUTIONS

1. Due to lanthanoid contraction, Zr and HF have nearly similar size *i.e.*, Zr (160 pm), Hf (159 pm), thus, they exhibit similar properties.

2. The complex of calcium with EDTA is used for the treatment of lead poisoning. Lead readily replaces calcium in the complex and lead-EDTA complex thus formed is finally eliminated from the body through urine.

3. High melting point (3410°C), moderate electrical resistance, low volatility, makes tungsten an important component in light bulbs.

4. EDTA is a hexadentate ligand, thus coordination number of Fe is 6 in [Fe(EDTA)].

5. (i) Optical isomerism
(ii) Geometrical isomerism

6. As strength of ligand increases crystal field splitting energy (CFSE) increases.

Order of strength of ligands :

$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < ox < H_2O < py = NH_3 < en < dipy < o\text{-phen} < NO_2^- < CN^- < CO$.

Now, $\Delta E = \dfrac{hc}{\lambda}$.

So, as CFSE increases, ΔE increases and λ decreases. Thus, the correct order of absorption of wavelength of light in the visible region is :

$[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

7. ScO_2^-; Group number = Oxidation state of Sc = 3.
TiO_3^{2-} : Group number = Oxidation state of Ti = 4
VO_3^- : Group number = Oxidation state of V = 5
$Cr_2O_7^{2-}$: Group number = Oxidation state of Cr = 6
CrO_4^{2-} : Group number = Oxidation state of Cr = 6
MnO_4^- : Group number = Oxidation state of Mn = 7

8. (a) $x + (-1) = +2$ or $x = +3$
(b) $x + 4(-1) = -2$ or $x = +2$
(c) $x + 3(-1) = 0$ or $x = +3$
(d) $x + 2(-1) = +1$ or $x = +3$

9. Atomic number (61) = $_{54}[Xe]\ 4f^5\ 6s^2$
Atomic number (91) = $_{86}[Rn]\ 5f^2\ 6d^1\ 7s^2$
Atomic number (101) = $_{86}[Rn]\ 5f^{13}\ 7s^2$
Atomic number (109) = $_{86}[Rn]\ 5f^{14}\ 6d^7\ 7s^2$

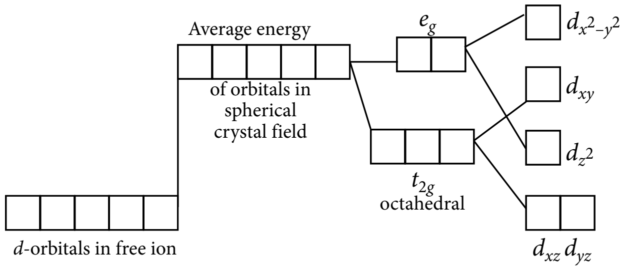
OR

(a) $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

(b) $Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$

10. The square planar arrangement can be derived from octahedral by removing two ligands from z-axis. On removing ligands from z-axis, d_{z^2}, d_{xz} and d_{yz} orbitals become more stable. As the lobes of $d_{x^2-y^2}$ point towards the ligands, the orbital has highest energy and the lobes of d_{xy} orbital lie

between the ligands, it is thus next highest orbital in energy. The lobes of d_{xz} and d_{yz} are least affected as they lie out of the plane of the complex. The d_{z^2} orbital is somewhat affected by electrostatic field of the ligands.

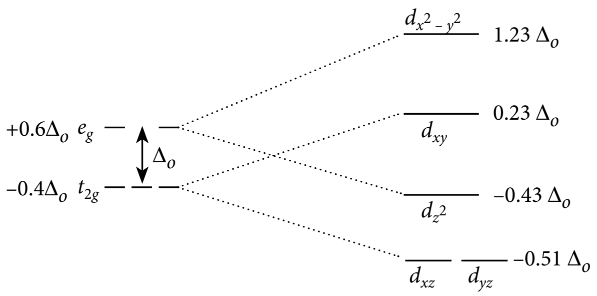


11. (i) The atomic radii of the third series of transition elements are virtually the same as those of the corresponding members of the second series due to lanthanoid contraction.

(ii) $Mn^{3+}(3d^4)$ is less stable than $Mn^{2+}(3d^5)$ which has stable half-filled configuration. Fe^{3+} is more stable than Fe^{2+} due to half-filled configuration. Cr^{3+} has stable t_{2g}^3 configuration. So, $E°$ value for the Mn^{3+}/Mn^{2+} couple is much more positive.

(iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride. Due to the high electronegativity and small size of oxygen and fluorine.

12. The terms "strong field" for square planar complexes means that the splitting of the two highest orbitals is greater than the pairing energy. Thus, the strong and weak field configurations are



CFSE (for strong field) $= 4(-0.51\Delta_o) + 2(-0.43\Delta_o) + 2(0.23\Delta_o) + P = -2.44\Delta_o + P$

CFSE (for weak field) $= 4(-0.51\Delta_o) + 2(-0.43\Delta_o) + 1(+0.23\Delta_o) + 1(+1.23\Delta_o) + P = -1.44\Delta_o + P$

13. (i) The most stable oxidation state of lanthanides is +3. Hence, ions in +2 state tend to change to +3 oxidation state by loss of electron and act as reducing agents.

(ii) La^{3+} has a stable configuration of an inert gas $[Xe]5d^06s^0$. To obtain +4 oxidation state, the stable configuration is to be disturbed which is not possible under ordinary conditions and hence, La^{4+} does not exist.

(iii) This is because gadolinium in +3 oxidation state has half filled 4f-subshell ($4f^{17}$) and lutetium in +3 state has completely filled 4f-subshell ($4f^{14}$) which are very stable configurations.

14. (a) Dicyano*bis*(ethylenediamine)cobalt(III) chlorate

(b) Potassium hexacyanocobaltate(II)

(c) Hexaamminenickel(II) hexanitrocobaltate(III)

15. +4 oxidation state : Cerium (Ce), Praseodymium (Pr), Terbium (Tb), Dysprosium (Dy)

+2 oxidation state : Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Thulium (Tm) and Ytterbium (Yb)

+4 and +2 oxidation states of lanthanoid elements arise mainly from the extra stability of empty, half-filled and fully-filled f-subshells. For example, Ce(IV) is $4f^0$ and has noble gas configuration. Similarly, Tb (IV) and Eu (II) have $4f^7$ configuration. Yb(II) has $4f^{14}$ configuration.

16. The given three coordination compounds are examples of special form of ionisation, called hydrate isomerism. Water can exist as a part of coordination entity or a part outside the coordination entity.

(a) $[Cr(H_2O)_6]Cl_3$: all three Cl^- ions are outside the coordination entity.

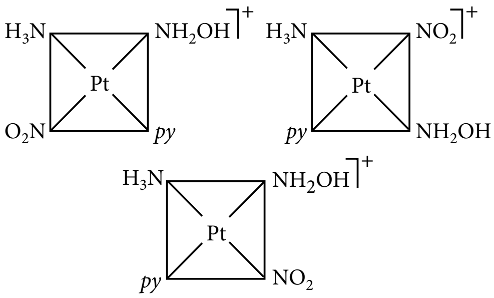
(b) $[CrCl(H_2O)_5]Cl_2{\cdot}H_2O$: one Cl^- ion is part of coordination entity and two are outside of it.

(c) $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$: two Cl^- ions are part of coordination entity and one is present outside of it.

The Cl^- ions outside the coordination entity are ionisable and forms white precipitate with $AgNO_3$ while Cl^- ions which are part of coordination entity are not ionisable.

OR

Three geometric isomers are possible for the given coordination compound. Any other possible configuration would merely be a rotation or reflection of one of these.



17. Small atoms like B, C, N, etc., can occupy positions in the voids among the atoms of transition metals. Such combinations are termed as interstitial compounds. They are usually non-stoichiometric materials having formulae like $VH_{0.56}$, $TiH_{1.7}$, TiC, etc.
Steel is an interstitial compound in which voids among iron atoms are occupied by carbon atoms.
Two important properties :
(i) Transition metals become more harder and rigid.
(ii) Melting points of interstitial compounds are higher than parent metals.

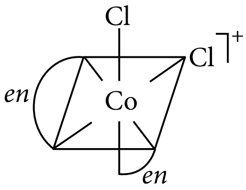
18. Calculate the magnetic moment by applying formula; $\mu = \sqrt{n(n+2)}$
(i) The magnetic moment of 1.7 B.M. corresponds to n = 1. Thus, in $K_4[Mn(CN)_6]$ there is only one unpaired electron in 3d-subshell. Thus, the distribution of five 3d-electrons in Mn(II) is $(t_{2g})^5$.
(ii) The magnetic moment of 4.9 B.M. indicates that there are four unpaired electrons in the complex. Thus, the six 3d-electrons in Fe(II) are distributed as $(t_{2g})^4\ (e_g)^2$.
(iii) The magnetic moment of 5.9 B.M. indicates that there are five unpaired electrons in the complex. Hence, the five 3d-electrons in Mn(II) are distributed as $(t_{2g})^3\ (e_g)^2$ in the given complex.

19. (i) Sc : $[Ar]3d^14s^2$, Sc^{3+} : [Ar] ;
It has no unpaired electron.
Cr : $[Ar]3d^54s^1$, Cr^{3+} : $[Ar]3d^3$;
It has three unpaired electrons. Hence, Cr^{3+} is paramagnetic.
(ii) V : $[Ar]3d^34s^2$, Mn : $[Ar]3d^54s^2$; Mn exhibits more number of oxidation states.
The expected oxidation states in V are +2, +3, +4, +5.
The expected oxidation states in Mn are +2, +3, +4, +5, +6, +7.
(iii) V^{4+} : [Ar] $3d^1$; One unpaired electron
V^{5+} : [Ar]; No unpaired electron
Hence, V^{5+} is diamagnetic in nature.

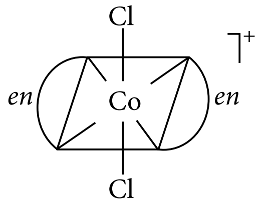
20. (i) Chlorophyll is a coordination compound of magnesium. Haemoglobin is a coordination compound of iron. Vitamin B_{12}, cyanocobalamine, the anti-pernicious anaemia factor, is a coordination compound of cobalt.
(ii) There is growing interest in the use of chelate therapy in medicinal chemistry. Excess of copper and iron are removed by the chelating ligands *D*-penicillamine and desferrioxime *B* via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours *e.g. cis*-platin.
(iii) Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands) as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α-nitroso-β-naphthol, etc.

21. All lanthanoids exhibit a common stable oxidation state of +3. In addition, some lanthanoids show +2 and +4 oxidation states also in solution or in solid compounds. These are shown by those elements which by doing so attain the stable f^0 (empty f-subshell), f^7 (half filled f-subshell) and f^{14} (fully filled f-subshell) configurations.
For example,
(i) Ce and Tb exhibit +4 oxidation state. Cerium (Ce) and terbium (Tb) attain f^0 and f^7 configurations respectively when they get +4 oxidation states, as shown below :
Ce^{4+} : $[Xe]4f^0$, Tb^{4+} : $[Xe]4f^7$
(ii) Eu and Yb exhibit +2 oxidation state. Europium and ytterbium get f^7 and f^{14} configurations in +2 oxidation states as shown below :
Eu^{2+} : $[Xe]4f^7$, Yb^{2+} : $[Xe]4f^{14}$

22. (a)

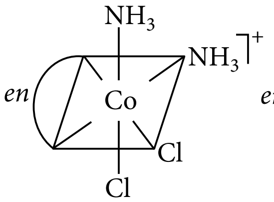


cis-form

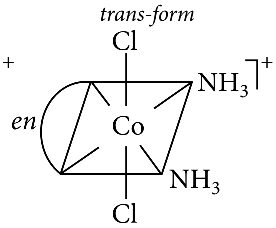


trans-form

(b)

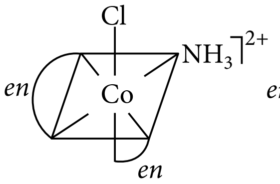


cis-form

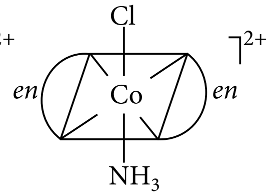


trans-form

(c)



cis-form



trans-form

23. (i) Oxidising property of $KMnO_4$ makes it a bleaching agent.

(ii) Reduction half reaction of $KMnO_4$ in acidic medium

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O, \quad E° = +1.52\ V$$

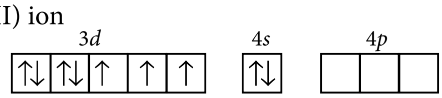
(iii) Chlorine may form some harmful compounds during bleaching of textiles. These compounds may cause water pollution whereas the bleaching by $KMnO_4$ is harmless.

(iv) Self awareness and concern towards environment.

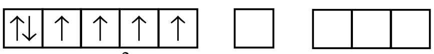
24. (a) (i) $[Co(NH_3)(Cl)(en)_2]^{2+}$

Name : Amminechloridobis(ethane-1, 2-diamine) cobalt(III) ion

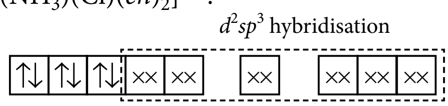
Co(27) :



Co(III) :



$[Co(NH_3)(Cl)(en)_2]^{2+}$:

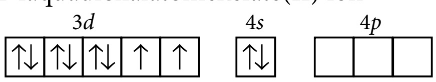


Since there are no unpaired electrons, complex is diamagnetic.

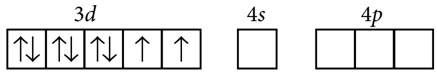
(ii) $[Ni(H_2O)_2(C_2O_4)_2]^{2-}$

Name : Diaquadioxalatonickelate(II) ion

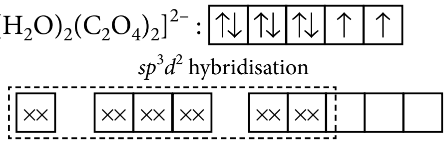
Ni(28) :



Ni(II) :



$[Ni(H_2O)_2(C_2O_4)_2]^{2-}$:



The complex has two unpaired electrons and therefore, it will be paramagnetic.

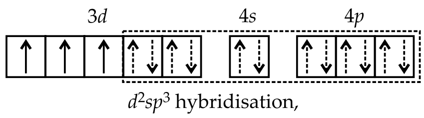
(b) $[Co(NH_3)(Cl)(en)_2]^{2+}$ is low spin complex and $[Ni(H_2O)_2(C_2O_4)_2]^{2-}$ is high spin complex.

OR

(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$

Oxidation state = +3, coordination number = 6

Electronic configuration : t_{2g}^3

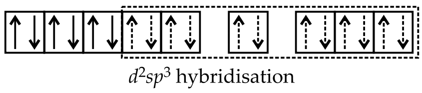


$$\mu = \sqrt{n(n+2)} = \sqrt{3\times 5} = \sqrt{15} = 3.87\ \text{B.M.}$$

(ii) $[Co(NH_3)_5Cl]Cl_2$

Oxidation state of Co = +3, coordination nubmer = 6

Electronic configuration : t_{2g}^6

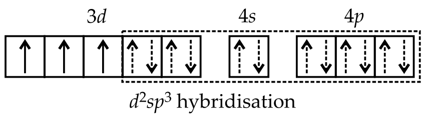


μ = 0 B.M.

(iii) $[CrCl_3(py)_3]$

Oxidation state = +3, coordination number = 6

Electronic configuration : t_{2g}^3

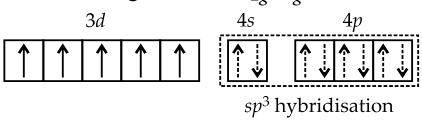


$$\mu = \sqrt{n(n+2)} = \sqrt{15} = 3.87\ \text{B.M.}$$

(iv) $Cs[FeCl_4]$

Oxidation state = +3, coordination number = 4

Electronic configuration : $t_{2g}^3\ e_g^2$

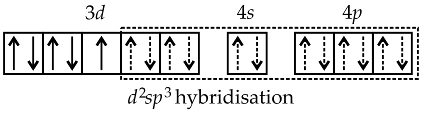


$$\mu = \sqrt{n(n+2)} = \sqrt{5\times 7} = \sqrt{35} = 5.92\ \text{B.M.}$$

(v) $K_4[Mn(CN)_6]$

Oxidation state = +2, coordination number = 6

Electronic configuration : t_{2g}^5



$\mu = \sqrt{n(n+2)} = \sqrt{1\times 3} = 1.732$ B.M.

25. (i) $\underset{(A)}{Ag_2S} + 4NaCN + 2O_2 \longrightarrow \underset{(B)}{2Na[Ag(CN)_2]} + \underset{(C)}{Na_2SO_4}$

(ii) $\underset{(B)}{2Na[Ag(CN)_2]} + Zn \longrightarrow Na_2[Zn(CN)_4] + \underset{(D)}{2Ag\downarrow}$

(iii) $\underset{(D)}{2Ag} + 4HNO_3 \longrightarrow 2AgNO_3 + 2NO_2 + 2H_2O$

$AgNO_3 + HCl \longrightarrow \underset{(E)}{AgCl\downarrow} + HNO_3$

(iv) $\underset{(E)}{2AgCl} + Na_2CO_3 \longrightarrow \underset{(D)}{2Ag} + 2NaCl + CO_2 + 1/2O_2$

(v) $\underset{(E)}{AgCl} + 2NH_4OH \longrightarrow \underset{(F)}{[Ag(NH_3)_2]Cl} + 2H_2O$

Thus, $A = Ag_2S$; $B = Na[Ag(CN)_2]$
$C = Na_2SO_4$; $D = Ag$; $E = AgCl$; $F = [Ag(NH_3)_2]Cl$

OR

(a) Copper has small size compared to alkali metals in their period. Its electronic configuration is $[Ar]3d^{10}4s^1$. As filled $3d$-subshell is less effective in shielding than s- and p-subshells, so s-electron in copper is more tightly held by the nucleus than that in alkali metals. Hence, its first ionisation energy is higher than for alkali metals. However, second and third ionisation energy values of copper are lower as compared to those of alkali metals due to removal of electrons from diffused d-orbitals.

(b) $4FeO\cdot Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow \underset{\substack{(A)\\ \text{Sodium chromate}\\ \text{(Yellow)}}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$

$\underset{\substack{(A)\\ \text{(Yellow)}}}{2Na_2CrO_4} + H_2SO_4 \longrightarrow \underset{\substack{(B)\\ \text{(Orange)}}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$

The compound (B) is oxidising agent.

26. (a) These complexes can ionise in solution as :
$[Co(NH_3)_3Cl_3]$ – does not ionise.
$[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$ (2 ions)
$[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$ (4 ions)
$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$ (3 ions)

As the number of ions in solution increases, their conductivity also increases. Therefore, conductivity follows the order :
$[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$

(b) The compounds having similar geometry may have different number of unpaired electrons due to the presence of weak and strong field ligands in complexes. If CFSE is high, the complex will show low value of magnetic moment and if CFSE is low, the complex will show high value of magnetic moment. For example, the $[CoF_6]^{3-}$ is paramagnetic but $[Co(NH_3)_6]^{3+}$ is diamagnetic.

(c) In $CuSO_4\cdot 5H_2O$, water acts as ligand. As a result it causes crystal field splitting. Hence, d-d transition is possible in $CuSO_4\cdot 5H_2O$ and shows colour. In the anhydrous $CuSO_4$ due to the absence of water (ligand), crystal field splitting is not possible and hence, no d-d transition occurs and shows no colour.

OR

(a) Lower wavelength is absorbed in octahedral complex than tetrahedral complex for the same metal and ligand. In tetrahedral coordination entity, formation of the d-orbital splitting is inverted and is smaller as compared to the octahedral field splitting. Thus, the energy of tetrahedral complex is smaller than compared to octahedral complex.
$\Delta_t = (4/9)\Delta_o$

(b) When white light falls on the complex, some part of it is absorbed. Higher the crystal field splitting, lower will be the wavelength absorbed by the complex. The observed colour of complex is the colour generated from the wavelength left over.

(c) $CoSO_4Cl\cdot 5NH_3$:

(i) Isomer A reacts with $AgNO_3$ but not with $BaCl_2$, it shows it has Cl^- ion outside the coordination sphere.
Hence, $A = [Co(NH_3)_5SO_4]Cl$
Isomer B reacts with $BaCl_2$ but not with $AgNO_3$, it shows it has SO_4^{2-} outside the coordination sphere.
Hence, $B = [Co(NH_3)_5Cl]SO_4$

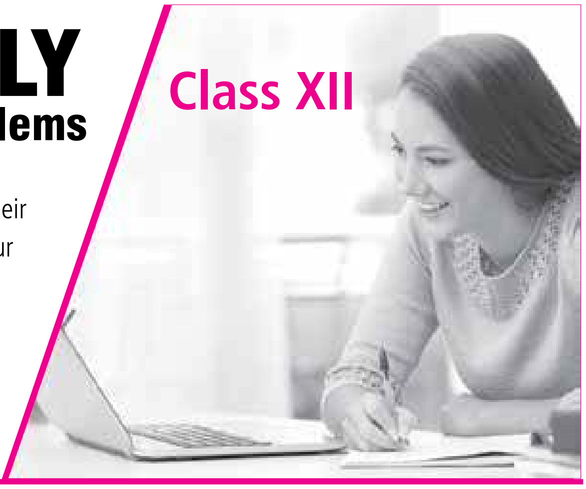
(ii) Ionisation isomerism

(iii) A = Pentaamminesulphatocobalt(III) chloride and
B = Pentaamminechlorocobalt(III) sulphate

◈◈

MPP-5 MONTHLY Practice Problems

Class XII



This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

The *d*- and *f*- Block Elements | Coordination Compounds

Total Marks : 120 **Time Taken : 60 Min.**

NEET / AIIMS

Only One Option Correct Type

1. The basic character of the transition metal monoxides follow the order
(a) CrO > VO > FeO > TiO
(b) TiO > VO >CrO > FeO
(c) TiO > FeO > VO > CrO
(d) VO > CrO > TiO > FeO

2. Which of the following statements is correct?
(a) Geometrical isomerism is not observed in complexes of coordination number four having tetrahedral geometry.
(b) Square planar complexes generally do not show geometrical isomerism.
(c) The square planar complexes of general formulae Ma_3b or Mab_3 exhibit *cis-trans* isomerism.
(d) The platinum glycinato complex, $[Pt(gly)_2]$ does not show geometrical isomerism.

3. There are three unpaired electrons in $[Co(H_2O)_6]^{2+}$ and calculated value of magnetic moment is 3.87 B.M which is quite different from the experimental value of 4.40 B.M. This is because of
(a) increase in number of unpaired electrons
(b) some contribution of the orbital motion of the electron to the magnetic moment
(c) change in orbital spin of the electron
(d) *d-d* transition.

4. In which of the following metal complexes, central metal atom have zero valency?
(a) $[Cu(NH_3)_4]SO_4$
(b) $K_3[Fe(CN)_6]$
(c) $[Ni(CO)_4]$
(d) $[Pt(NH_3)_2Cl_2]$

5. If zinc pieces are added to $FeCl_3$ solution, its colour changes from yellow to light green. It is because
(a) $FeCl_3$ solution is acidic due to hydrolysis and zinc added produces nascent hydrogen causing reduction of $FeCl_3$ to $FeCl_2$
(b) $FeCl_3$ solution is basic and zinc added produces H_2 which reduces $FeCl_3$ to $FeCl_2$
(c) zinc oxidises $FeCl_3$ to $FeCl_2$
(d) none of the above is correct.

6. The two compounds pentaamminesulphato-cobalt(III) bromide and pentaamminesulphato-cobalt(III) chloride represent
(a) linkage isomerism
(b) ionisation isomerism
(c) coordination isomerism
(d) none of these.

7. Which compound is coloured due to charge transfer spectra?
(a) $K_2Cr_2O_7$
(b) $KMnO_4$
(c) CrO_3
(d) All of these

8. Crystal field stabilisation energies of octahedral and tetrahedral complexes having high spin d^6 configuration respectively are
(a) $0.6\ \Delta_o$, $0.6\ \Delta_t$
(b) $0.4\ \Delta_o$, $0.4\ \Delta_t$
(c) $0.4\ \Delta_o$, $0.6\ \Delta_t$
(d) $0.6\ \Delta_o$, $0.4\ \Delta_t$

9. Pick out the correct statements from the following :
(1) Cobalt(III) is more stable in octahedral complexes.
(2) Zinc forms coloured complexes.
(3) Most of the *d*-block elements and their compounds are ferromagnetic.
(4) Osmium shows +8 oxidation state.

(5) Cobalt (II) is more stable in octahedral complexes.
(a) 1 and 2 (b) 1 and 3
(c) 2 and 5 (d) 1 and 4

10. Which of the following characteristics is true for $[Ni(en)_2]^{2+}$ complex?
(a) Paramagnetism, dsp^2, square planar, coordination number of Ni = 2
(b) Diamagnetism, dsp^2, square planar, coordination number of Ni = 4
(c) Diamagnetism, sp^3, tetrahedral, coordination number of Ni = 4
(d) Paramagnetism, sp^3, tetrahedral, coordination number of Ni = 4

11. On heating $KMnO_4$, which one among the following is not formed?
(a) K_2MnO_4 (b) O_2
(c) MnO_2 (d) MnO

12. Choose the correct name for $[Co(NH_3)_5Cl]Cl_2$.
(a) Pentaamminechlorocobalt(II) chloride
(b) Pentaamminechlorocobalt(III) chloride
(c) Pentaamminechlorocobalt(III) dichloride
(d) Pentaamminecobalt(III) chloride

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. Assertion : $KMnO_4$ is stored in dark coloured bottles.
Reason : On heating with alkalies, $KMnO_4$ is converted to manganate.

14. Assertion : F^- ion is a weak ligand and forms outer orbital complex.
Reason : F^- ion cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals of the same shell.

15. Assertion : There is an increase in oxidation potential of Fe^{2+} when it combines with a ligand CN^-.
Reason : Ionic activity of Fe^{2+} increases during complex formation of $[Fe(CN)_6]^{4-}$.

JEE MAIN / JEE ADVANCED

Only One Option Correct Type

16. A complex containing Mn^{2+} and Br^- ions was found to have a magnetic moment of 5.92 B.M. The probable formula and geometry of the complex is most likely to be
(a) $[MnBr_4]^{2-}$, tetrahedral
(b) $[MnBr_6]^{3-}$, octahedral
(c) $[MnBr_4]^{2-}$, square planar
(d) $[MnBr_5]^{3-}$, trigonal planar

17. Which of the following orders are correct?
(I) $5d-5d > 4d-4d > 3d-3d$ (orbital overlapping)
(II) $Mn^{2+} > Fe^{2+} > Cr^{3+} > Cu^{2+}$ (magnetic moment)
(III) $Sc^{3+} > Zn^{2+} > V^{5+} > Ti^{4+}$ (magnetic nature)
(IV) Zn > Cu > Fe > Co (atomic size)
(a) Only I, II (b) Only I, IV
(c) Only I, II, IV (d) Only II, III, IV

18. On treatment of $[Pt(NH_3)_4]^{2+}$ with concentrated HCl, two compounds (I) and (II) having the same formula, $[Pt(NH_3)_2Cl_2]$ are obtained, (I) can be converted into (II) by boiling with dilute HCl. A solution of (I) reacts with oxalic acid to form $[Pt(NH_3)_2(C_2O_4)]$ whereas (II) does not react. Choose the correct option from the following :
(a) (I) *cis*, (II) *trans*; both tetrahedral
(b) (I) *cis*, (II) *trans*; both square planar
(c) (I) *trans*, (II) *cis*; both tetrahedral
(d) (I) *trans*, (II) *cis*; both square planar

19. $FeCr_2O_4$ (chromite) is converted to Cr by the following steps :

$$\text{Chromite} \xrightarrow{\text{I}} Na_2CrO_4 \xrightarrow{\text{II}} Cr_2O_3 \xrightarrow{\text{III}} Cr$$

I, II and III are

	I	II	III
(a)	Na_2CO_3/air, Δ	C	C
(b)	NaOH/air, Δ	C, Δ	Al, Δ
(c)	NaOH/air, Δ	C, Δ	Mg, Δ
(d)	conc. H_2SO_4, Δ	NH_4Cl, Δ	C, Δ

More than One Options Correct Type

20. $K_4[Fe(CN)_6]$ is used in the identification of
(a) Fe^{2+} ions (b) Fe^{3+} ions
(c) Cu^{2+} ions (d) Cd^{2+} ions.

21. Mark the incorrect statements.
(a) Potassium dichromate oxidises a secondary alcohol into a ketone.
(b) Potassium permanganate is a weaker oxidising agent than potassium dichromate.
(c) Potassium permanganate is a stronger oxidising agent than potassium dichromate.
(d) Potassium dichromate oxidises a secondary alcohol into a aldehyde.

22. In basic medium, the amount of Ni^{2+} in a solution can be estimated with the dimethylglyoxime reagent. The correct statements about the reaction and the product are
(a) in ammoniacal solution, Ni^{2+} salts give cherry-red precipitate of nickel(II) dimethylglyoximate
(b) two dimethylglyoximate units are bound to one Ni^{2+}
(c) in the complex, two dimethylglyoximate units are hydrogen bonded to each other
(d) each dimethylglyoximate unit forms a six-membered chelate ring with Ni^{2+}.

23. When an acidified dichromate solution is shaken with a pinch of Na_2O_2
(a) a blue colouration is observed
(b) orange red colouration finally changes to green
(c) oxygen gas is evolved
(d) bluish green precipitate is formed.

Integer Answer Type

24. The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride, is close to

25. Amongst the following, the number of metals which do not form amalgams is
Ti, V, Cr Mn, Fe, Co, Ni, Pt, Cu, Zn

26. The complex, $Ca_2[M(CN)_6]$ has spin only magnetic moment 2.83 B.M. and the complex $K_2[MCl_4]$ has spin only magnetic moment of 4.9 B.M. How many electrons are present in valence shell *d*-orbitals of the neutral gaseous atom *M*?

Comprehension Type

The lanthanoids exhibit a principal oxidation state of +3. The +3 oxidation states in lanthanum, gadolinium and lutetium are stable because these ions have an empty, a half-filled and completely filled 4*f*-subshell respectively. But some of the lanthanoids exhibit different oxidation states.

27. Good oxidising agent out of the following lanthanoids is
(a) Ce^{3+} (b) Sm^{2+}
(c) Ce^{4+} (d) Eu^{2+}

28. For which of the following lanthanoids, +2 oxidation state exists in aqueous solution?
(a) Ce,Yb, La (b) Ce, Eu, Ho
(c) Er, Tb, Sm (d) Sm, Eu, Yb

Matrix Match Type

29. Match the magnetic moments listed in Column II with the electronic configurations of the complexes listed in Column I and choose the correct option using the codes given below.

Column I	Column II
(A) d^3 (octahedral)	(p) 0.0 B.M.
(B) d^5 (octahedral, low spin)	(q) $2\sqrt{6}$ B.M.
(C) d^6 (octahedral, low spin)	(r) $\sqrt{15}$ B.M.
(D) d^6 (octahedral, outer orbital)	(s) $\sqrt{3}$ B.M.

	A	B	C	D
(a)	p	r	q	s
(b)	r	s	p	q
(c)	r	p	q	s
(d)	q	r	p	s

30. Match the Column I with Column II and choose the correct option using the codes given below.

Column I	Column II
(A) Aquated Mn^{2+} ion	(p) White
(B) $FeSO_4 \cdot 7H_2O$	(q) Blue
(C) Aquated V^{4+} ion	(r) Pink
(D) Anhydrous $CuSO_4$	(s) Green

	A	B	C	D
(a)	p	q	r	s
(b)	p	s	q	r
(c)	r	s	q	p
(d)	q	p	r	s

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Keys are published in this issue. Search now! ☺

SELF CHECK

No. of questions attempted ……
No. of questions correct ……
Marks scored in percentage ……

Check your score! If your score is

> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

CHEMISTRY MUSING

PROBLEM SET 50

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET

1. A cylinder of gas is assumed to contain 11.2 kg of butane. If a normal family needs 20,000 kJ of energy per day for cooking, how long will the cylinder last? (Given : the heat of combustion of butane is 2658 kJ mol^{-1})

(a) 27 days (b) 3700 min
(c) 26 days (d) 5000 s

2. The equilibrium constant K_p for the reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

is 1.64×10^{-4} at 400 °C. What will be the equilibrium constant at 500 °C if the heat of reaction in this temperature range is –25,140 calories?

(a) 1.4×10^{-5} (b) 3.6×10^{-6}
(c) 2.8×10^{-10} (d) 10^{-10}

3. $\underset{(A)}{PhMe} \xrightarrow[H_3O^+]{KMnO_4/OH^-} (B) \xrightarrow[\text{or } PCl_5]{SOCl_2} (C) \xrightarrow{PhCOONa} (D)$

Compound (*D*) is

(a) PhCOCl (b) $PhCONH_2$
(c) PhCOOH (d) $(PhCO)_2O$

4. Two compounds have the empirical formula, $Cr(NH_3)_3(NO_2)_3$. In aqueous solution, one of these conducts electricity while the other does not. What is the probable structure of the compound which conducts electricity?

(a) $[Cr(NH_3)_3(NO_2)_3]$ (b) $[Cr(NH_3)_2(NO_2)_3]NH_3$
(c) $[Cr(H_2O)(NH_3)_3(NO_2)_2]NO_2$
(d) None of these

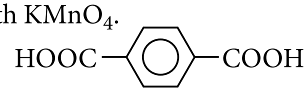
5. Choose the correct arrangement of the following in decreasing order of $\left(\frac{m}{o+p}\right)$ ratio.

I. $PhCH_3$ II. $PhCBr_3$
III. $PhCCl_3$ IV. $PhCl_3$

(a) II > III > I > IV (b) IV > II > III > I
(c) III > II > I > IV (d) I > III > II > IV

JEE ADVANCED

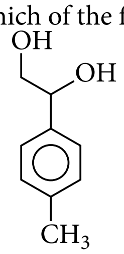
6. An optically active compound (*A*) of formula, $C_9H_{12}O_2$ produced the following compound when refluxed with $KMnO_4$.

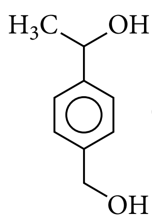


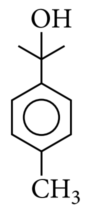
The original compound showed these properties also :

$$\underset{(A)}{C_9H_{12}O_2} \begin{cases} \xrightarrow{Na} H_2 \text{ liberated} \\ \xrightarrow{Br_2} \text{no rapid reaction} \\ \xrightarrow[\text{cool}]{CrO_3/H^+} C_9H_8O_3 \end{cases}$$

Which of the following is the structure of (*A*)?

(a) 

(b) 

(c) 

(d) both (a) and (b)

COMPREHENSION

A yellow powder *X* is burnt in a stream of fluorine to obtain a colourless gas, *Y* which is thermally stable and chemically inert. Its molecule has octahedral geometry. Another colourless gas, *Z* with same constituent atoms as that of *Y* is obtained when sulphur dichloride is heated with sodium fluoride. Its molecule has trigonal bipyramidal geometry.

7. The yellow powder *X* is

(a) $K_2Cr_2O_7$ (b) $FeCl_3$
(c) K_2CrO_4 (d) S

8. The colourless gases *Y* and *Z* respectively are

(a) SF_4, SF_4 (b) SF_6, SF_4
(c) NaF, SF_6 (d) S_2F_2, NaF

INTEGER VALUE

9. Total number of aldol condensation products of the following reaction is

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\Delta]{KOH_{(aq)}}$$

10. The reaction, $SO_2Cl_2 \xrightarrow{k_1} SO_2 + Cl_2$ is a first order reaction with $k_1 = 2.2 \times 10^{-5}\ sec^{-1}$ at 302 °C. The percentage of SO_2Cl_2 that will get decomposed in 90 minutes when the reaction is carried out at 302 °C is (8.2 + *y*). The value of *y* is

◆◆

JEE Advanced

PRACTICE PROBLEMS

SECTION 1 (Maximum Marks : 18)

This section contains 6 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct. For each question you will be awarded 3 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.

1. The enthalpy changes at 298 K in successive breaking of O—H bonds of HOH are

$H_2O_{(g)} \longrightarrow H_{(g)} + OH_{(g)}$; $\Delta H = 498$ kJ mol^{-1}

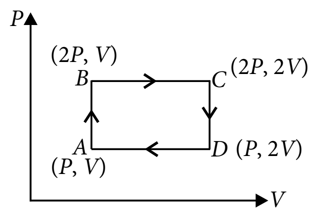
$OH_{(g)} \longrightarrow H_{(g)} + O_{(g)}$; $\Delta H = 428$ kJ mol^{-1}

The bond enthalpy of O—H bond is

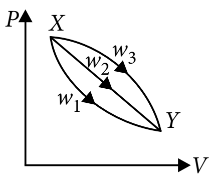
(a) 498 kJ mol^{-1} (b) 463 kJ mol^{-1}
(c) 428 kJ mol^{-1} (d) 70 kJ mol^{-1}

2. An ideal monoatomic gas is taken round the cycle $ABCDA$ as shown in the figure. The work done during the cycle is

(a) $-PV$
(b) $-2PV$
(c) $-\frac{1}{2}PV$
(d) zero.



3. A given mass of gas expands from the state X to state Y by three paths 1, 2 and 3 as shown in the figure. If w_1, w_2 and w_3 respectively be the work done by the gas along these three paths then



(a) $w_1 > w_2 > w_3$ (b) $w_2 < w_1 < w_3$
(c) $w_1 = w_2 = w_3$ (d) $w_1 < w_2 < w_3$

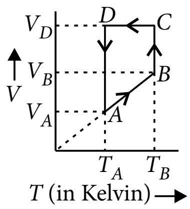
4. Identify the reaction in which the heat liberated corresponds to the heat of formation (ΔH).

(a) $C_{(diamond)} + O_{2(g)} \rightarrow CO_{2(g)}$ + heat
(b) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$ + heat
(c) $C_{(diamond)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ + heat
(d) $S_{(rhombic)} + O_{2(g)} \rightarrow SO_{2(g)}$ + heat

5. The entropy change in the fusion of one mole of a solid melting at 27°C is (latent heat of fusion = 2930 J mol^{-1})

(a) 9.77 J K^{-1} mol^{-1} (b) 10.73 J K^{-1} mol^{-1}
(c) 2930 J K^{-1} mol^{-1} (d) 108.5 J K^{-1} mol^{-1}

6. Two moles of a monoatomic ideal gas are taken through a cyclic process starting from A as shown in the figure. The volume ratios are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27 °C, calculate the total heat absorbed (in calories) in the cyclic process.



(a) 1080 (b) 900 (c) 600 (d) 1200

SECTION 2 (Maximum Marks : 08)

This section contains 2 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which one or more than one answer is correct. For each question you will be awarded 4 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marking in this section.

7. Five moles of an ideal gas at 293 K are expanded isothermally from an initial pressure of 0.4 kPa to a final pressure of 0.1 kPa against a constant external pressure of 0.1 kPa. Select the correct option(s).

(a) $q = 0$ and $w \neq 0$
(b) $q = 0$ and $w = 0$
(c) $\Delta E = 0$ and $\Delta H \neq 0$
(d) $\Delta E = 0$ and $\Delta H = 0$

8. In an insulated container, 1 mole of a liquid (molar volume 100 mL) at 1 bar is steeply taken to 100 bar when volume of liquid decreases by 1 mL. Select the correct option(s).

(a) $\Delta U = 99$ bar mL (b) $\Delta U = 100$ bar mL
(c) $\Delta H = 9900$ bar mL (d) $\Delta H = 100$ bar mL

By : **Vidyalankar Institute**, Pearl Centre, Senapati Bapat Marg, Dadar (W), Mumbai - 28. Tel.: (022) 24306367

SECTION 3 (Maximum Marks : 24)

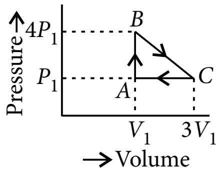
This section contains 6 integer type questions. Answers have to be given in between 0 to 9 in the form of nearest integer. Each question carries 4 marks if you have darkened the correct answer and no negative mark will be awarded for an incorrectly bubbled answer.

9. 3.5 g of a gas (mol. wt. = 28) was burnt in excess of oxygen at 298 K in a constant volume calorimeter. The temperature of the calorimeter was found to increase to 298.45 K. The enthalpy of combustion (in kJ mol^{-1}) is (Heat capacity of calorimeter = 2.5 kJ K^{-1})

10. The heat of formation of ethane is –19.46 kcal. Bond energies of H—H, C—H and C—C bonds are 104.18, 99.0 and 80.0 kcal respectively. The heat of atomization of graphite can be expressed in scientific notation as $p \times 10^q$ calories. Identify p.

11. For a hypothetical reaction, $A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$ $\Delta G°$ and $\Delta S°$ are 20 kJ/mol and –20 J K^{-1} mol^{-1} respectively at 200 K. If ΔC_p is 20 J K^{-1} mol^{-1} then $\Delta H°$ at 400 K is x. Find $\frac{x}{4}$?

12. An ideal gas is taken around the cycle $ABCA$ as shown in the figure. Work done in the cyclic process = xP_1V_1. What is the value of x ?



13. In a thermodynamic process, helium gas obeys the law $\frac{T}{P^{2/5}}$ = constant. The heat given to n moles of He in order to raise the temperature from T to $2T$ is

14. In the process :
$H_2O_{(s)}$ (–10 °C, 1 atm) $\rightarrow$ $H_2O_{(l)}$ (10 °C, 1 atm)
C_p for ice = 9 cal deg^{-1} mol^{-1},
C_p for H_2O = 18 cal deg^{-1} mol^{-1}
Latent heat of fusion of ice = 1440 cal mol^{-1} at 0 °C
The entropy change for the above process will be

SECTION 4 (Maximum Marks : 06)

This section contains 1 paragraph. Based upon paragraph, 2 multiple choice questions have to be answered. For each question you will be awarded 3 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.

PARAGRAPH

Chemical reactions can be viewed from a thermodynamic perspective. Change in enthalpy (ΔH) and entropy (ΔS) are the two driving forces that determine whether a reaction is spontaneous. Gibbs free energy (ΔG) combines these two factors in one equation :

$$\Delta G = \Delta H - T\Delta S$$

Compound	$\Delta H_f°$(kJ/mol)	$S°$(J/mol–K)
$N_{2(g)}$	0	192
$H_{2(g)}$	0	131
$NH_{3(g)}$	–46	192

15. What is the value of $\Delta H°$ for the reaction, $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$?

(a) –46 kJ (b) –92,000 J
(c) 0 J (d) 138 kJ

16. What is $\Delta S°$ for the reaction, $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$?

(a) –201 J/K (b) –192 J/K
(c) –131 J/K (d) 201 J/K

SECTION 5 (Maximum Marks : 16)

This section contains 2 questions. Each question contains statements given in 2 columns. Statements in the first column have to be matched with statements in the second column. For each question in this section, you will be awarded 8 marks if you have darkened all the bubbles corresponding only to the correct answer and 2 marks for each row. No negative mark will be awarded for an incorrectly bubbled answer.

17. Match the Column I with Column II.

Column I	Column II
(A) Ice $\rightleftharpoons H_2O_{(l)}$ at room temperature 25 °C	(p) ΔH = –ve, ΔS = +ve
(B) $H_2O_{(l)} \rightleftharpoons$ Ice at room temperature 25°C	(q) ΔG = +ve
(C) $2O_{3(g)} \rightarrow 3O_{2(g)}$	(r) ΔH = +ve, ΔS = –ve
(D) $3O_{2(g)} \rightarrow 2O_{3(g)}$	(s) ΔG = –ve

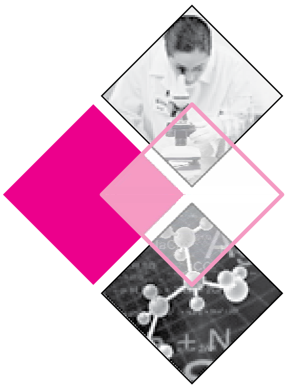
18. Match the Column I with Column II.

Column I	Column II
(A) Ice $\rightleftharpoons$ Water at 273 K	(p) $\Delta H < 0$, $\Delta S < 0$
(B) $NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$	(q) $\Delta G = 0$
(C) $2NH_{3(g)} \rightarrow 3H_{2(g)} + N_{2(g)}$	(r) $\Delta n > 0$, $\Delta H > \Delta U$
(D) $CO_{2(g)} \rightarrow$ Dry ice	(s) $\Delta n < 0$, $\Delta H < \Delta U$

ANSWER KEY

1. (b) **2.** (a) **3.** (d) **4.** (d) **5.** (a)
6. (d) **7.** (d) **8.** (b, c) **9.** (9) **10.** (2)
11. (5) **12.** (3) **13.** (0) **14.** (6) **15.** (b)
16. (a) **17.** (A) - (s), (B) - (q), (C) - (p, s); (D) - (q, r)
18. (A) - (q), (B) - (p, s), (C) - (r); (D) - (p, s)

For detailed solutions to the JEE Advanced Practice Problems visit our website: www.vidyalankar.org



CONCEPT BOOSTER

Hi all!! Hope you all are doing well. This is the last part of the consecutive 'SHORTCUT OF INORGANIC CHEMISTRY' article. Inorganic Chemistry is endless but what I have tried is to give you an idea, how to read Inorganic Chemistry. Hope you liked it. Keep practicing harder and harder.

*Arunava Sarkar

HEATING EFFECTS

HEATING EFFECT OF DICHROMATE SALTS

$$2K_2Cr_2O_7 \xrightarrow{\Delta} \underset{\text{yellow}}{2K_2CrO_4} + \underset{\text{green}}{Cr_2O_3} + \frac{3}{2}O_2\uparrow$$

HEATING EFFECT OF PHOSPHATE SALTS

Shortcut : Remove only water and if any gas is possible (like NH_3 but not O_2 and oxides of P) then that too.

- Now, phosphoric acid is H_3PO_4. So, the first salt that comes to our mind is NaH_2PO_4 (one acidic hydrogen substitution). It is 1° phosphate salt.

  $$NaH_2PO_4 \xrightarrow{\Delta} H_2O + NaPO_3$$

  (Just remove H_2O; don't think much.)

  $$2Na_2HPO_4 \xrightarrow{\Delta} H_2O + Na_4P_2O_7$$

  $Na_3PO_4 \xrightarrow{\Delta}$ no effect as there is no water molecule to be removed.

- Ammonium containing phosphate salts, of course evolve NH_3 along with water on heating.

  For example,

  $$2Mg(NH_4)PO_4 \xrightarrow[\text{(NH}_3\text{, water removal)}]{\Delta} Mg_2P_2O_7 + 2NH_3 + H_2O$$

  $$Na(NH_4)HPO_4{\cdot}4H_2O \xrightarrow[-4H_2O]{\Delta} Na(NH_4)HPO_4 \xrightarrow{\Delta} NaH_2PO_4 + NH_3$$

  $$NaH_2PO_4 + NH_3 \xrightarrow{\Delta} \underset{\text{(already discussed)}}{H_2O + NaPO_3}$$

HEATING EFFECT OF OXALATE SALTS

- In general, more reactive metal's oxalate salts give both CO and CO_2 on heating whereas less reactive metals give CO_2 only.

  $$FeC_2O_4 \xrightarrow{\Delta} FeO + CO + CO_2$$

  $$SnC_2O_4 \xrightarrow{\Delta} SnO + CO + CO_2$$

  $$7Na_2C_2O_4 \xrightarrow{\Delta} 7Na_2CO_3 + 2CO_2 + 3CO + 2C$$

  (It is interesting!! Keep in mind)

  $$\left.\begin{array}{l} Ag_2C_2O_4 \xrightarrow{\Delta} 2Ag + 2CO_2 \\ HgC_2O_4 \xrightarrow{\Delta} Hg + 2CO_2 \end{array}\right\} \text{Again the shortcut for Ag and Hg works.}$$

HEATING EFFECT OF ACETATE SALTS

A few points must be remembered here :

- Formation of acetone is inevitable as this is a general method of preparation of acetone.
- Smaller alkaline earth metals like Be, Mg (first two in the group) cannot hold bigger CO_3^{2-} tightly with them and they prefer to exist in the form of oxide. So, for them, metal oxide and CO_2 will be produced. But, for relatively larger metals like Ca, Ba, etc. carbonate salts will be produced.
- For alkali metals, carbonate salts are obtained.

Let us check :

$$(CH_3COO)_2Ca \xrightarrow{\Delta} CaCO_3 + CH_3COCH_3$$

$$(CH_3COO)_2Ba \xrightarrow{\Delta} BaCO_3 + CH_3COCH_3$$

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$$\mathrm{Mg}\begin{array}{l}\diagup OCOCH_3\\ \diagdown OCOCH_3\end{array} \xrightarrow{\Delta} MgO + CO_2 + CH_3COCH_3$$

$$\mathrm{Be}\begin{array}{l}\diagup OCOCH_3\\ \diagdown OCOCH_3\end{array} \xrightarrow{\Delta} BeO + CO_2 + CH_3COCH_3$$

$$\mathrm{Pb}\begin{array}{l}\diagup OCOCH_3\\ \diagdown OCOCH_3\end{array} \xrightarrow{\Delta} PbO + CO_2 + CH_3COCH_3$$

$$2CH_3COONa \xrightarrow{\Delta} Na_2CO_3 + CH_3COCH_3$$

$$2CH_3COOK \xrightarrow{\Delta} K_2CO_3 + CH_3COCH_3$$

HEATING EFFECT OF FORMATE SALTS

Three major points to be remembered :

- Lower alkali metals give corresponding oxalates.
- Alkaline earth metals give formaldehyde (in general).
- Silver and mercury salts as usual give metal back along with formic acid. Let us see :

$$2HCOONa \xrightarrow{300°\text{-}350°C} \begin{array}{c}COONa\\ |\\ COONa\end{array} + H_2\uparrow$$

$$2HCOOAg \xrightarrow{\Delta} HCOOH + 2Ag + CO_2$$

$$(HCOO)_2Hg \xrightarrow{\Delta} HCOOH + Hg + CO_2$$

HEATING EFFECT OF BORIC ACID

- $$4H_3BO_3 \xrightarrow[(-4H_2O)]{100°C} 4HBO_2 \xrightarrow[-H_2O]{145°C} H_2B_4O_7 \xrightarrow[> 400°C]{\text{Red hot}} H_2O + 2B_2O_3$$

HEATING EFFECT OF OXALIC ACID

- $$\begin{array}{c}COOH\\ |\\ COOH\end{array} \xrightarrow{\Delta} CO + CO_2 + H_2O$$

◇◇

MPP-5 CLASS XII ANSWER KEY

1.	(b)	2.	(a)	3.	(b)	4.	(c)	5.	(a)
6.	(d)	7.	(d)	8.	(c)	9.	(d)	10.	(b)
11.	(d)	12.	(b)	13.	(b)	14.	(a)	15.	(c)
16.	(a)	17.	(c)	18.	(b)	19.	(b)	20.	(b,c)
21.	(b,d)	22.	(a,b,c)	23.	(a,b,c)	24.	(6)	25.	(2)
26.	(5)	27.	(c)	28.	(d)	29.	(b)	30.	(c)

ADVANCED CHEMISTRY BLOC

(AN INSIGHT TO MOT)

Mukul C. Ray, Odisha

LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

The definition goes like this.

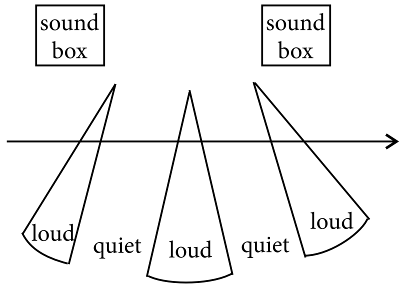
"The simplest trial functions that work reasonably well in molecular orbital theory turn out to be linear combination of atomic orbitals, or LCAO".

But what is the trial function? In molecular orbital theory (MOT), you actually do not solve Schrödinger (ö is a German umlaut, read it as Schroedinger) equation. It's not that easy. Instead you use a trial function, an "educated guess" as to what the solution might be. Suppose you want to know the value of x in the equation, $4x + 5 = 70$ without solving. Without solving you just guess a value of x and see how it works. In MOT, the estimating procedure is analogous. In order to determine how well a trial function for an orbital works in MOT, you calculate energy. Your trial wave function should try to approach as close as to the energy of the actual orbital. In MOT, the trial wave function for molecular orbitals are weighted linear sum of valence atomic orbitals of atoms in a molecule. When I say weighted that means you need not necessarily take equal contribution of atomic orbital wave functions of combining atoms.

Number of atomic orbitals combining is equal to the number of molecular orbitals formed. It's not new, I am sure, for you that is atomic orbitals combine to give $\sigma 1s$ and $\sigma^* 1s$, former having lower energy and later higher energy than combining atomic orbitals.

In VBT, we treat electrons as if they reside in the atomic orbital. This is an over simplification. We tried in a better way in MOT. The bonding molecular orbital arises out of constructive interference between the atomic orbitals because both orbitals have the same phase. The antibonding orbital arises out of destructive interference.

You can compare the situation like the following :



Say, you are walking along the arrow mark you will be able to notice remarkably neat pattern of alternating maxima and minima produced from two identical sources. This is superposition of waves from two loud speakers. The atomic orbital wave functions almost behave similarly.

The key point to understand is that, every electron which enters a bonding molecular orbital stabilises the molecule or polyatomic ion and every electron which enters an antibonding molecular orbital destabilises it. The emphasis on electron pair has been removed.

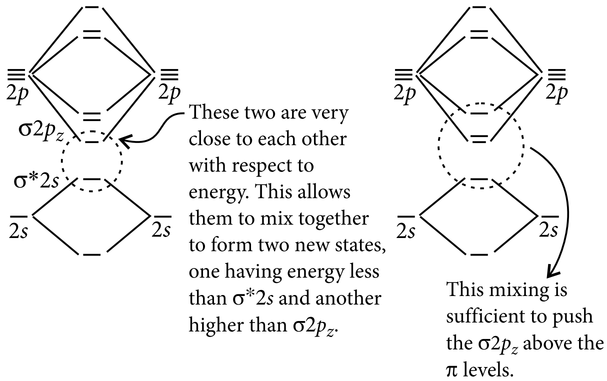
Also, an electron when removed from bonding orbital, destabilises the system and an electron when added to antibonding orbital also destabilises the system but adding an electron to antibonding orbital destabilises it more.

Applications

- Stability : $H_2 > H_2^+ > H_2^-$

  Even though the bond order of H_2^+ and H_2^- are same, H_2^- is less stable. The paragraph just above explains this observation.

- For second period diatomic molecules, O_2 and F_2, the sequence of energy of molecular orbital is $(\sigma 2s)\,(\sigma^*2s)\,(\sigma 2p_z)\,(\pi 2p_x = \pi 2p_y)\,(\pi^*2p_x = \pi^*2p_y)\,(\sigma^*2p_z)$ It's simple to handle, O_2, O_2^+, O_2^-, O_2^{2-}, F_2, etc. You just feel the electrons from lower end considering each molecular orbital takes maximum 2 electrons and for degenerate molecular orbital, Hund's rule is applicable.
- For second period diatomic molecules on the left of oxygen like B_2, C_2, N_2, the energy sequence is slightly altered. The reason is that the energy gap between $2s$ and $2p$ is less in these atoms B, C, N, etc.



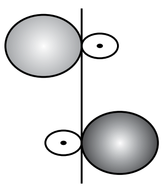
(MO energy order of B_2, C_2, N_2, etc.)

Also you must note the stability sequence :

$N_2 > N_2^+ > N_2^-$

The explanation is the same as for H_2^+ and H_2^-.

- For CO, the two hybrid orbitals are directed at 180° to each other.



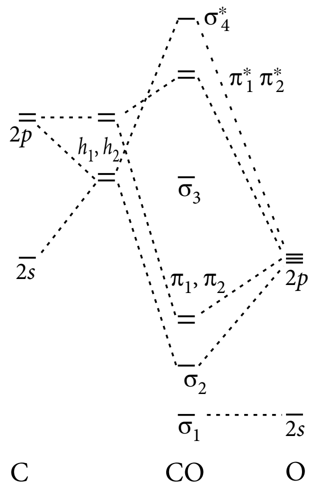
carbon centre
(Two sp hybrids, h_1 and h_2)

Solution Senders of Chemistry Musing

Set - 49

- Ravinder Kashapogu, Telangana
- Naveen Soni, Gujarat
- Akila Iyer, Bengaluru

One hybrid orbital is directed dimetrically opposite to the CO bonding region. Hence, it does not form bond but retains a pair of electron (σ_3).



σ_3 is primarily of non-bonding nature. The pair of electrons present in σ_3 is the carbon based lone pair, which is approximately 126 pm far from carbon in opposite direction to oxygen. This lowers the dipole moment of CO molecule significantly down to 0.112 D.

When CO ionises to CO^+, the carbon-oxygen bond length decreases from 112.8 pm to 111.5 pm. Some author have an opinion that bond order has increased from 3 to 3.5 in CO^+. But this is not very reasonable as second period elements can never form more than three bonds. (Though Re forms quadruple bond in $Re_2Cl_8^{2-}$ ion). The better explanation comes from VBT. A triple bond that has partial dative bond character develops pure covalent character in order to distribute the net positive charge on both the atoms. As an evidence, we can see that dative bonds are longer than isoelectronic covalent bonds. For example,

$\ddot{N}\equiv\ddot{N}$ (14 e^-)	109.4 pm
$:C\overset{\leftarrow}{\equiv}\ddot{O}$ (14 e^-)	112.8 pm

Also,

CH_3-CH_3 (18 e^-)	153.4 pm
$H_3N\rightarrow BH_3$ (18 e^-)	156 pm

So, when the dative bond of CO changes to covalent bond in CO^+, the bond length decreases.

CHEMISTRY MUSING

SOLUTION SET 49

1. (a) : Let radius of hollow sphere X be r.

$\therefore$ Edge length $(a) = 4r/\sqrt{3}$

Volume of unit cell $= a^3 = (4r/\sqrt{3})^3$

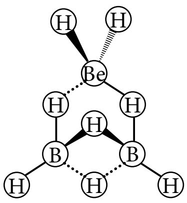
Volume of X unoccupied by Y (having radius $= r/2$)

in unit cell $= 2\times\left[\frac{4}{3}\pi r^3 - \frac{4}{3}\pi\left(\frac{r}{2}\right)^3\right]$

$$\therefore \frac{\text{Volume of } X \text{ unoccupied by } Y \text{ in unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{\frac{4}{3}\pi\times\frac{7r^3}{8}\times 2}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{7\pi\sqrt{3}}{64}$$

2. (c) :



P = Be

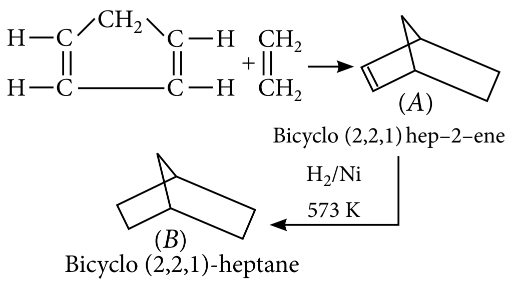
Q = B

3. (d) : Cu^{2+} (X) $\xrightarrow{\text{NaOH}}$ $Cu(OH)_2$ Blue ppt. (Y)

Cu^{2+} (X) $\xrightarrow{\text{NaOH in presence of tartaric acid}}$ Fehling solution (Deep blue solution) $\xrightarrow{HCOO^-Na^+}$ Cu_2O (Z) Red ppt.

Formic acid is different from other monocarboxylic acids as it can act as a reducing agent, thus it reduces Fehling solution to red cuprous oxide.

4. (b) :



5. (c) : $BOH + HCl \rightarrow BCl + H_2O$

At equivalence point, $M_1V_1 = M_2V_2$

$\frac{2}{5}\times 2.5 = \frac{2}{15}\times V_2$, $V_2 = 7.5$ mL, $V_{HCl} = 7.5$ mL

Moles of BOH in 2.5 mL = 0.001

Moles of HCl in 7.5 mL = 0.001

$\therefore$ Moles of salt formed = 0.001

Total volume = 2.5 + 7.5 = 10 mL = 0.01 L

Conc. of salt $= \frac{0.001}{0.01} = 0.1$ mole/litre

Hydrolysis of salt takes place:

$$pH = 7 - \frac{1}{2}(pK_b + \log C)$$

$$pH = 7 - \frac{1}{2}(12 - 1)$$

$[\because pK_b = -\log 10^{-12} = 12 \text{ and } \log 0.1 = -1]$

pH = 1.5 $\Rightarrow$ $-\log[H^+] = 1.5$

$\Rightarrow \log[H^+] = -1.5$

$[H^+] = 3.2\times 10^{-2}$ M

6. (d) : 374 kJ is required for 1 mole

$\therefore$ 22.44 kJ is required for $= \frac{1}{374}\times 22.44$ moles $= 0.06$

$$\text{Moles} = \frac{\text{mass}}{\text{Atomic mass}}$$

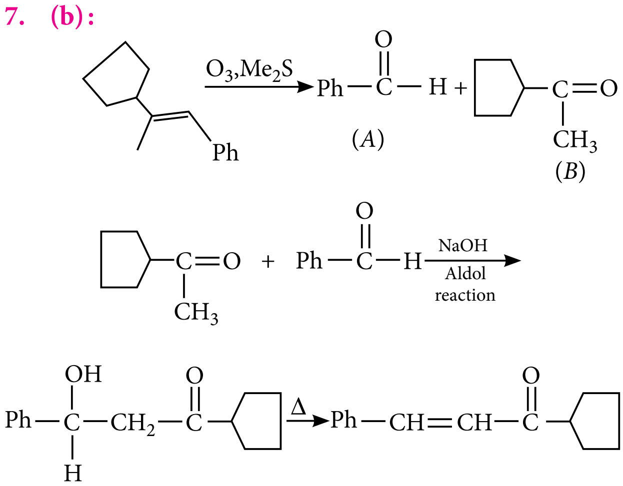
$0.06 = \frac{8}{\text{Atomic mass}}$, Atomic mass = 133.33

Moles of $M^+_{(g)}$ formed = 0.06

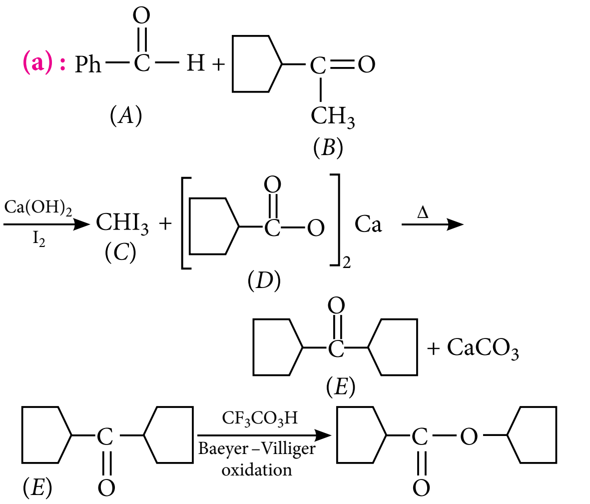
Thus, atoms of M converted to $M^+_{(g)} = 0.06\times 6.023\times 10^{23}$

$= 3.613\times 10^{22}$ atoms

7. (b) :



8. (a):



9. (2): $K_f = \frac{\Delta T_f}{i \cdot m} = \frac{0.704}{2 \times 0.1892}$ ($\because$ KCN dissociates completely, $i = 2$)

$= 1.86 \text{ K Kg mol}^{-1}$

	$Hg(CN)_2$ +	xCN^- $\rightarrow$	$[Hg(CN)_{x+2}]^{x-}$
Initial moles:	0.095	0.1892	0
Final moles:	0	$(0.1892 - 0.095\,x)$	0.095

Total molality after the addition of $Hg(CN)_2$

= molality of K^+ + molality of CN^- + molality of $[Hg(CN)_{x+2}]^{x-}$

$= 0.1892 + (0.1892 - 0.095x) + 0.095$

$= (0.4734 - 0.095\,x)$

Now, $K_f = \frac{\Delta T_f}{m} \Rightarrow 1.86 = \frac{0.53}{0.4734 - 0.095\,x}$

$x = 2.$

10. (2): The kinetic energy of the electron is provided by accelerating potential,

$$V = \frac{h^2}{\lambda^2 \times 2 \times e \times m}$$

$\lambda = 8.7 \text{ pm} = 8.7 \times 10^{-12}$ m

$e = 1.6 \times 10^{-19}$ C,

$m = 9.1 \times 10^{-31}$ kg

$h = 6.63 \times 10^{-34}$ J s

$$V = \frac{(6.63 \times 10^{-34} \text{ J s})^2}{(8.7 \times 10^{-12} \text{ m})^2 \times 2 \times (1.6 \times 10^{-19} \text{ C}) \times 9.1 \times 10^{-31} \text{ kg}}$$

$= 1.99 \times 10^4 \text{ kg m}^2 \text{ s}^{-2} \text{ C} \approx 2 \times 10^4$ V

CROSS WORD

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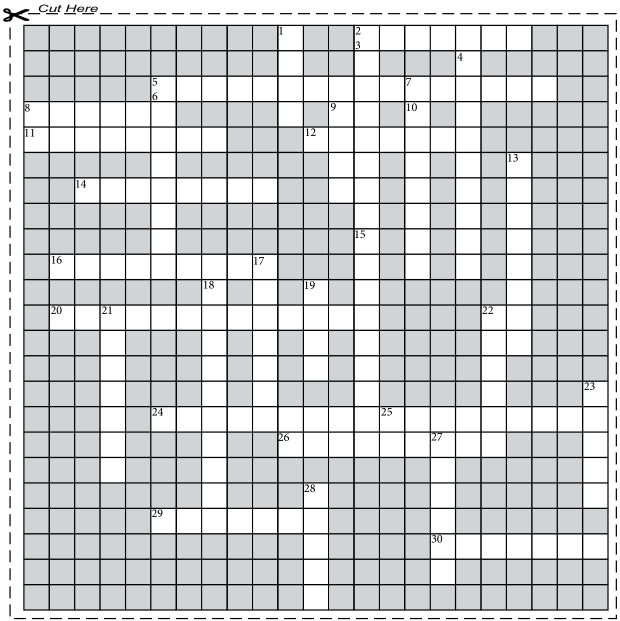

ACROSS

3. A mildly toxic, white crystalline organic compound belonging to the indole family. It occurs naturally in faeces and coal tar and has a strong faecal odour. (7)
6. An aminopyridine that functions as a centrally acting non-opioid analgesic that was originally used as an analgesic for acute and chronic pain. (10)
7. A gelatinous precipitate formed by coagulation of a sol. (6)
8. A German scientist who prepared almost perfectly semipermeable membrane using gelatinous copper ferrocyanide, $Cu_2[Fe(CN)_6]$. (6)
11. Naturally occurring alloy of gold and silver (upto 45% Ag). It resembles pure gold in appearance. (8)
12. An atomic unit of energy which is equal to e^2/a_0 (where e is the charge of an electron and a_0 is the atomic unit of length). (7)
14. An arsenic derivative that causes blisters and used in chemical warfare. (8)
16. An instrument used to determine fermentation efficiency of yeast by measuring the amount of carbon dioxide produced from a given quantity of sugar. (9)
20. The action of heating a substance until it burns away rapidly. (12)
24. _______ law which expresses the dependence of a reaction enthalpy on temperature. (9)
25. A stable heterocyclic octacirculene based on thiophene. (9)
26. A polycyclic alkane with a structure similar to basket. (9)
29. Fraction which is defined as the mass defect divided by the mass number. (7)
30. A mineral deposit of gravel, sand and nitrates, found in dry areas of America. (7)

DOWN

1. Small, granular, opaque diamonds, used as an abrasive in cutting tools. (4)
2. The contraction of a gel accompanied by the separating out of liquid. (9)
4. A technique in which a stable atom in a compound is replaced by its radioactive isotope. (9)
5. _______ include all quarks and leptons, as well as any composite particle made of an odd number of these, such as all baryons and many atoms and nuclei. (8)
9. A metal oxide obtained by heating an ore to high temperature in air. (4)
10. A reactor which produces more fissile nuclei than it consumes. (7)
13. A thermodynamic property of a real gas which is effective partial pressure. (8)
15. Polymethine fibre with elastic properties. (7)
17. Equation which gives relation between effect of temperature on surface tension. (6)
18. A mixture of two or more components that reaches an equilibrium temperature which is independent of the temperature of any of its components before they are mixed. (10)
19. The rule which is a practical aid for determining the configuration of chiral centers of amino acids. (4)
21. An organothiophosphate insecticide primarily used on corn. (7)
22. An analogue of pyrrole in which an arsenic atom replaces the nitrogen atom. (6)
23. The tendency of a solid material to move slowly or deform permanently under the influence of mechanical stress. (5)
27. A general name for alloys containing Al, Ni, Co and Fe, used as permanent magnets. (6)
28. A very hard natural form of silica, used for knife-edges of balances and in ornaments. (5)

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